Semiconductor detector for the selective detection of atomic hydrogen

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A semiconductor detector is described which responds to the atomic hydrogen in an atomic beam but is insensitive to molecular hydrogen. The hydrogen flux is measured through the change in conductivity of the semiconductor material which occurs when the hydrogen is chemisorbed. The atomic flux from a rf hydrogen discharge is used to determine the sensitivity of the detector. The minimum detectable signal is $\sim 10^9$ hydrogen atoms $mm^{-2}\,s^{-1}$. The detector has a response time of less than 2 ms.

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INTRODUCTION

A new detector for the measurement of atomic hydrogen flux has been developed. The response of the detector is assumed to arise from the change in conductivity when hydrogen becomes chemisorbed to its surface. The detector is highly sensitive to atomic hydrogen, $\sim 10^9$ atoms $mm^{-2}\,s^{-1}$, but insensitive to molecular hydrogen. The response time, ~ 2 ms, is much faster than comparable detection schemes. Quantitative measurements of atomic fluxes are possible. The sensitivity of the detector is stable and it is not seriously affected by pressure cycling. The VUV radiation from the hydrogen source produces no measureable signal. In addition the small size of the detector element allows good geometrical resolution of beam profiles. Finally, since the apparatus is simple and the detector element itself is commercially available, this approach provides an extremely convenient method for the selective, quantitative measurement of atomic hydrogen flux in hydrogen beams, as well as other applications such as the regulation of flux in hydrogen masers.

There are a number of other techniques for the measurement of hydrogen flux. The heat of recombination of atomic to molecular hydrogen can be measured with a bolometer.[1] This allows the absolute flux to be obtained with good sensitivity but response times are long and the geometry of the detector is awkward for obtaining beam cross sections. Semiconductor bolometers operated at low temperatures have been used to detect hydrogen by recombination.[2] These have high sensitivity and fast response but must be operated at very low temperatures and are not completely selective. Another approach is to use compression tubes with pressure gauges but the selectivity to atomic hydrogen alone is lost. By using a mass spectrograph one obtains very high sensitivity but absolute calibration and beam profile measurements become difficult.[3] The conductivity of a MoO_3 film which changes chemically when exposed to atomic hydrogen has been used to measure hydrogen flux with high sensitivity.[4] However, the film eventually saturates and must be renewed by reoxidation or baking. Similarly, the surface conductivity of a single ZnO crystal was used to quantitatively and selectively measure hydrogen flux.[5] Here the hydrogen is chemisorbed to the crystal surface and increases its surface conductivity. However, the surface becomes saturated and must be repeatedly baked to be regenerated.

In this paper, the properties of a new semiconductor detector are first discussed. Then the vacuum apparatus for producing and measuring the hydrogen beam and the electronic bridge which allows the change in conductivity to be measured are described. The sensitivity of the detector is estimated from a hydrogen beam profile measured experimentally. Finally, the response of the detector to vacuum ultraviolet radiation, visible, and infrared radiation is presented and the response mechanism to atomic hydrogen is discussed.

I. EXPERIMENTAL ARRANGEMENT

A. Detector properties

The semiconductor material used in this work is a commercially available, thick-film thermistor material.[6] It is a sintered combination of nickel oxide, manganese oxide, and cobalt oxide.[7] This dense polycrystalline solid is composed of crystalline grains with dimensions of about 1 μ. It has a high surface-to-mass ratio with a body structure allowing 20% voids. The oxide film used in this experiment has a front surface area 1.0×1.0 mm and is 50 μ thick. The mass was measured to be 0.5 mg. The heat capacity of this material is $3.8 \times 10^{-4}\,J\,g^{-1}\,K^{-1}$.[7] Since the material was intended for use as a temperature sensor, it has a high-temperature coefficient of resistance α, where $\alpha = (1/R)(dR/dT)$ and R is the resistance and T is the temperature. For this oxide film $\alpha = -4 \times 10^{-2}\,K^{-1}$ at 300 K.

The detector has two platinum electrodes on opposite edges of one face. Electrical connections are attached to its corners by four platinum wires, 18 μ in diameter. These wires are 1.8 mm in length and are connected to four posts of a standard TO-5 header. This provides a very convenient method to both handle the film as well as to make electrical connections. The resistance of the detector in this configuration is approximately 6 MΩ.

B. Atomic-beam apparatus

The measurements which determined the characteristics of the hydrogen detector were performed in a stainless-

steel vacuum chamber with inner dimensions of 69-cm length, 30-cm width, and 21-cm depth. An oil-free pumping system was used to produce and maintain a vacuum in order to reduce surface contamination. A moderate vacuum was produced by two Varian Vacsorb rough pumps. These were then valved off and a high vacuum was maintained by a Varian Model VK-12C cryopump. The cryopump has a rated speed for hydrogen of 1000 l/s. A typical base vacuum was 3×10^{-8} Torr. The pressure was measured with an ionization gauge.

The hydrogen beam is produced in a rf discharge at one end of the vacuum chamber. A schematic diagram of the beam apparatus is shown in Fig. 1. The hydrogen is filtered and regulated by a palladium leak and then introduced into a Pyrex bulb 4.0 cm in diameter. Electrodes surrounding the bulb couple in approximately 25 W of rf power at 70 MHz which dissociates the molecular hydrogen. The atomic hydrogen then effuses through a Pyrex capillary 1.0 mm in diameter and 2.0 cm long to form the beam. By knowing the speed of the pumps and the conductivity of the capillary tube for hydrogen, the operating pressure of the hydrogen discharge was determined. For the measurements presented here the discharge pressure was 7.5 μ. In this regime the mean-free path of the gas is approximately the length of the capillary. It is thus possible to calculate the beam flux on the beam axis in either of the limits where the capillary is transparent or is opaque to collisions for the atoms effusing through it.[8] In both cases, the result on the beam axis is 10^{12} atoms/s for a solid angle of 2×10^{-5} sr which is the angle subtended by the detector. Beyond the capillary collimator a pair of electrodes having an applied voltage difference of 67 V sweep away any ions which enter the beam from the discharge.

A chopper for the atomic beam is located 15 cm from the hydrogen source. This interrupts the beam at 22 Hz to form a nearly square-wave modulation. The chopper blades are magnetically coupled to a motor on the exterior of the vacuum chamber. A reference signal is provided for synchronous detection. By employing phase-sensitive detection, ambient temperature drifts are eliminated from the detector signal.

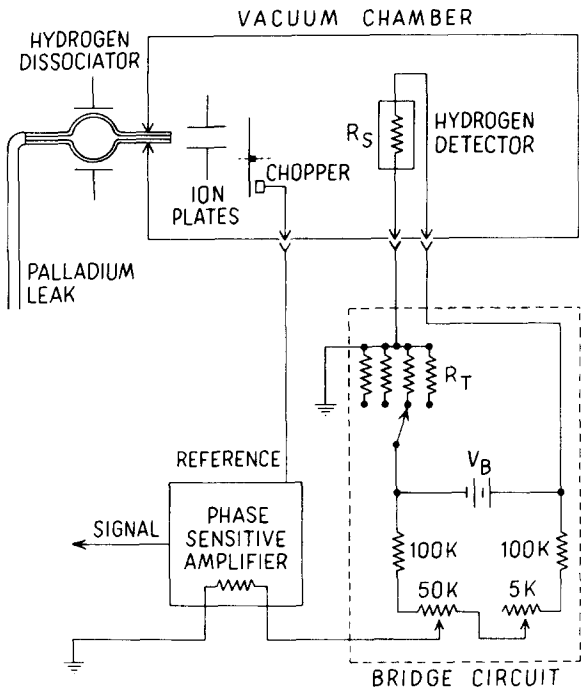

FIG. 1. Schematic diagram of the atomic beam and resistance bridge.

The detector is housed in a heavy aluminum block which acts as a heat sink. The block is attached to a carriage which may be moved with precision on a dovetail slide rail approximately 3.5 cm to either side of the center of the atomic beam. The detector element is 22 cm from the end of the collimating capillary. The leads from the TO-5 case were connected by a shielded cable to a BNC feedthrough on the wall of the chamber.

C. Resistance bridge

Because changes in the conductivity of the detector element are to be monitored, it is desirable to use a simple Wheatstone resistance bridge and phase-sensitive detector as shown in Fig. 1. The bridge is balanced by first selecting a resistance R_T which approximately equals the resistance R_S of the detector element. The output is then nulled coarsely by adjusting the 50-KΩ potentiometer and finely nulled by adjusting the 5-KΩ potentiometer. The resistors are precision 1% types and the potentiometers are ten-turn precision types. The bridge voltage is provided by V_B. The transfer function for the above arrangement is simply

$$\Delta V_S = [R_T V_B/(R_S + R_T)^2](\Delta R_S), \tag{1}$$

where ΔV_S is the bridge imbalance voltage and ΔR_S is the change in resistance of the detector. For the results presented here, $R_S = 5.9$ MΩ, $R_T = 3.0$M Ω, and $V_B = 45.7$ V. Since the impedance of the bridge is large it is straightforward to match it to amplifiers with a good noise figure. The output of the bridge and the reference from the chopper are sent to a phase-sensitive amplifier. This has an input bandpass filter with 3-dB cutoff at 5 and 100 Hz. The output signal has a filter bandwidth of 0.8 Hz.

II. MEASUREMENTS

Using the arrangement just described, the properties of the detector element, in particular its response to atomic hydrogen, were measured quantitatively. When the system was first pumped down, the resistance of the semiconductor film began to increase. From its initial value of 1.0 MΩ it eventually reached approximately 6 MΩ where it was fairly stable. This change is attributed to outgassing of the material, particularly at intergrain boundaries. The resistance changed reversibly by as much as 1 MΩ when the chamber was let up to air. This is attributed to thermal and chemisorption effects. The detector was directly exposed to the hydrogen beam and the sign of the voltage change from the bridge indicated that the conductivity increased when atomic hydrogen impinged on the detector element. By observing the output of the bridge with an oscilloscope when the beam was being chopped, the detector response was found to be faster than 2 ms. This is much faster than the thermal re-

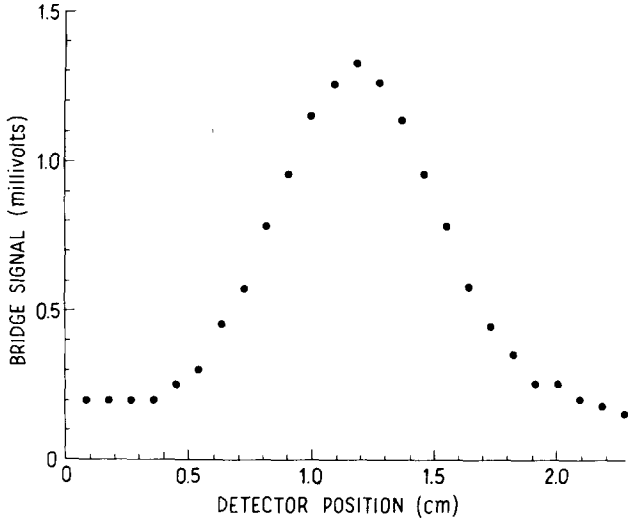

FIG. 2. Profile of the atomic hydrogen beam. The signal is taken from the output of the phase-sensitive detector. The beam width is approximately 7.3 mm.

sponse of the element when acting as a bolometer. This was measured to be approximately 5 s by exposing the detector under vacuum to a step function of blackbody radiation.

The profile of the hydrogen beam was measured by translating the detector on its carriage along the dovetail slide. The results are shown in Fig. 2. The full width at half-maximum of the atomic beam is 7.3 mm. This is almost twice the collimation, i.e., half the beam width, that one would expect from a long collimating channel.[8] This may be explained by assuming a high degree of recombination on the walls of the capillary. In this case the beam is determined by two collimating apertures which are the entrance and the exit areas of the capillary.[9]

The response of the detector was also determined. Correcting for the filtering and calibration of the phase-sensitive detector, the bridge voltage on the beam axis was 2.4 mV for a flux of 1×10^{12} atoms/s. This estimated flux is calculated from the chamber pressure and the pumping speed. If the pumping speed is less than estimated or if the beam is incompletely dissociated, the atomic flux would be smaller and the sensitivity of the detector greater. The sensitivity given here may, therefore, be taken as the minimum sensitivity possible. When the atomic beam was blocked the rms noise background indicated by the phase-sensitive detector was 5 μV. This yields a signal to noise of 46 dB in the present case and an estimated minimum detectable signal of 5×10^{9} atoms/s assuming the device is linear. The above limit is probably due to $1/f$ noise and may be reduced by operating at a higher chopping frequency. The voltage change stated above and shown in Fig. 2 indicates by Eq. (1) a resistance change of 1.4 KΩ.

III. DETECTOR RESPONSE

The change in conductivity in the metal oxide detector element could arise from sources other than the neutral atomic hydrogen beam. Infrared radiation causes heating of the element and hence a change in its resistance. Visible, ultraviolet, or vacuum ultraviolet radiation could have a photoconductive effect. Alternatively, the atoms could produce an effect through the kinetic energy of fast neutrals or ions, molecular recombination, or chemisorption. It is therefore desirable to isolate the source and nature of the response of the detector. The hydrogen signal is characterized by the restriction that it produce a beam profile similar to Fig. 2.

The hydrogen source might produce a collimated beam of infrared radiation which mimics the signal. To eliminate this possibility a NaCl crystal 3-mm thick was placed in front of the detector element. NaCl transmits radiation from 0.2 to 15 μ. Thus, blackbody radiation at room temperature, which peaks at 9 μ, or higher temperatures would be transmitted, but an atomic beam would not. When a beam profile was measured with this arrangement no signal was observed. Similarly, the hydrogen discharge may produce radiation from the hydrogen spectrum which is then collimated by the capillary nozzle. This ranges in wavelength from the Lyman series in the vacuum ultraviolet through the visible into the infrared. An effect could be produced in the detector if the metal oxide is sufficiently photoconductive. A crystal of MgF_2 1-mm thick transmits radiation from 1200 Å to 7 μ. However, when this crystal was placed in front of the detector, no beam profile could be measured. From the above it is clear that the effect arises from the particle flux and not from radiation.

When the atomic hydrogen in the beam strikes the detector element, it may stay long enough to recombine with another hydrogen atom to form molecular hydrogen. The binding energy of the molecule is 4.476 eV so that this exothermic reaction is capable of heating the detector. The temperature increase of the semiconductor element which is caused by hydrogen recombination may be calculated by assuming a uniform temperature distribution on the detector in which the heat flux from the beam is balanced by conduction through radiation and the support wires. The result for the temperature change ΔT for an energy flux ΔW is[7]

$$\Delta T = \epsilon \Delta W / G(1+\omega^2\tau^2)^{1/2}, \tag{2}$$

where ϵ is the recombination efficiency of hydrogen on the substrate, G is the effective thermal conductance which takes into account the change of Ohmic heating with temperature, ω is the angular frequency at which ΔW is modulated, and τ is the thermal time constant of the detector. The thermal time constant is given by $\tau = C/G$, where C is the heat capacity of the detector element. One may use Eq. (2) to find the temperature change for a given heat flux. Then using Eq. (1) and the thermal coefficient for the semiconductor, the bridge voltage may be found. For the atomic flux encountered in this work, it is found that if $\epsilon = 0.5$, the signal expected from the phase-sensitive detector is approximately 1 μV, much smaller than the measured signal. On the other hand, the thermal time constant τ is calculated to be 9 s which is near the measured time of 5 s, indicating the validity of the approach which was used.

The atomic hydrogen beam may also affect the conductivity of the metal oxide through chemisorption. In this phenomenon, when the hydrogen atom comes in contact with the oxide surface it is chemically bound while molecu-

lar hydrogen is not. The electron from the atom is transferred to a surface state in the semiconductor to form an accumulation layer. This layer is characterized by an excess density of electrons which leads to an increase in conductivity of the semiconductor. This phenomenon has been observed in ZnO (Ref. 5) and SnO_2 which have band gaps of 3.2 and 3.5 eV, respectively. The material used here consists predominantly of NiO which has a band gap of approximately 4.0 eV. One would expect these materials to behave similarly. However, the response time of the detector described above is much faster than previous versions with a single crystal of ZnO.[5] This may be due to rapid recombination on the currently used oxide layer. When hydrogen is chemisorbed it may diffuse across the surface of the metal oxide. If it encounters a recombination center (a metal cluster, for instance) it may efficiently form molecular hydrogen which is weakly bound. This mechanism, or one similar, could prevent the surface from saturating. In the limit of rapid recombination or weak binding it is found that the number of chemisorbed atoms is directly proportional to the incident flux.[5,10] The response time of the detector, therefore, may be adjusted by heating or cooling the substrate. Furthermore, the sintered material used here should be appreciably more sensitive than a single large crystal. The individual crystals are connected by narrow channels after sintering. If the hydrogen is chemisorbed at these channels, their effect is augmented since the ratio of surface area to volume is largest there. In addition, the nature of sintering provides a relatively large surface area to improve the dynamic range of the detector. The linearity of this device was not measured. However, because of the effects just mentioned, the saturation flux would probably occur for an atomic beam orders of magnitude more intense than the one used here. It is possible that the detector can be used to detect atomic oxygen. In this case, when oxygen is chemisorbed it would form a depletion layer which would decrease the conductivity of the detector.

The semiconductor detector described in this work provides an extremely convenient method to selectively detect atomic hydrogen. Further improvements which increase the relative surface area but maintain the fast response time seem possible.

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