Development of a Hydrogen Detector for use in Coal Mines

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Summary

Transmission of light through a palladium film changes when the film is exposed to and absorbs hydrogen. The changing transmission can be related to the hydrogen concentration and forms the basis for a hydrogen sensor. To be useful in coal mines, the hydrogen sensor must be capable of detecting percentage concentrations of hydrogen in the presence of approximately equal concentrations of carbon monoxide. Unfortunately, at room temperature, carbon monoxide is adsorbed onto the surface of palladium films reducing the rate of hydrogen absorption (and hence sensor response rate) to unacceptable levels.

It has been found that by heating the palladium film, carbon monoxide adsorption decreases and hydrogen absorption (sensor response) is again rapid and reproducible, though reduced in magnitude. At elevated temperatures the palladium film "oxidises" with time and this alters its response characteristics. Coating of the palladium film with gold has been has been effective in preventing oxidation, however the benefits are only short-term. Palladium alloys and alternate diffusion barriers offer the possibility of longer term solutions.

Introduction

Post-explosion mine atmospheres can contain percentage levels of carbon monoxide and hydrogen which are formed by the partial combustion of methane according to the equation:

$$2\,CH_4 + O_2 \rightarrow 2\,CO + 4\,H_2$$

The presence of hydrogen is of particular concern because of its wide flammable range (4-74%) and its relatively low ignition temperature. Currently there are no hand-held hydrogen detectors suitable for use in coal mines which can measure percentage concentrations of hydrogen. The objective of this project was to develop such a detector, that is one which can accurately determine hydrogen concentrations in the range 0-5% in the presence of percentage levels of carbon monoxide.

Palladium and Hydrogen

The presence of hydrogen in a palladium film raises the Fermi level thereby decreasing the proportion of electrons which may be excited by absorbing light. This results in less light absorption and hence greater transmission. This change in transmission with film hydrogen content forms the basis of our hydrogen sensor.

Palladium has a face centred cubic structure in which hydrogen atoms have an unusually high solubility and mobility. The phase diagram for hydrogen/palladium (Figure 1) shows that at room temperature when the hydrogen partial pressure exceeds approximately 0.02 atm there is a dramatic increase in hydrogen solubility which is the result of the α-β phase transition of the palladium. There is an accompanying change in film transmission and thus maximum sensitivity to changes in hydrogen pressure are obtained in the region of the phase transition. Unfortunately the palladium crystal structure also changes with the phase transition so that measurements in the transition region can result in permanent deformation of the palladium structure (1,2). This can lead to sensor hysteresis.
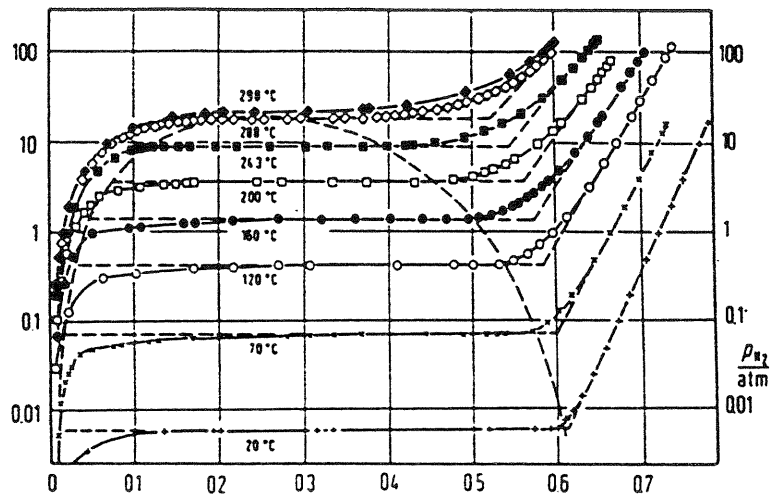
Figures 1. Hydrogen palladium isotherms (3)

As temperature increases higher hydrogen partial pressures are required to bring about the phase transition (Figure 2) so that at 80°C, a hydrogen partial pressure of approximately 0.1 atm is required. Thus increasing temperature moves the phase transition outside the measuring range of interest (0-0.04 atm, that is 0-4% hydrogen).
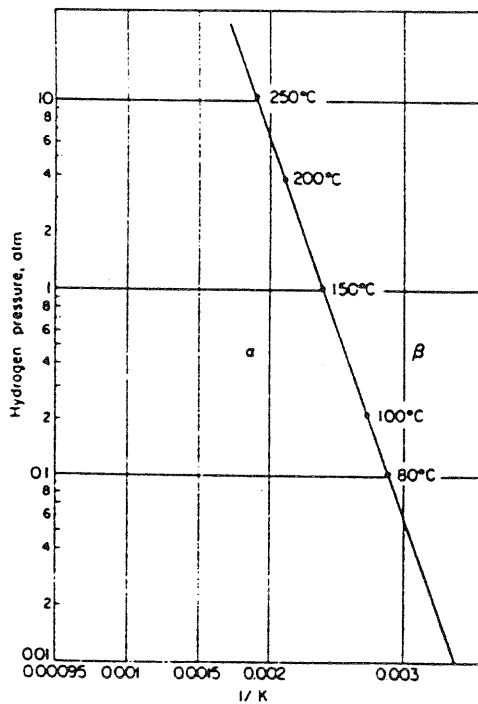

Figure 2.   α-β phase transitions with respect to hydrogen pressure and temperature. (4)

Hydrogen Sensor

In its initial configuration (Figure 3) the hydrogen sensor consisted of a piece of Corning 7059 glass approximately 25mm x 10mm x 1.1mm thick coated with a thin (~ 15 microns) film of palladium produced by R.F. Magnetron sputtering. Corning 7059 glass was chosen because it is essentially sodium free. It had been found that if "normal" soda-lime glass was used, diffusion of sodium into the palladium deactivated the film. To provide a "reference" whose transmission did not change on exposure to hydrogen, one end of the film was covered with a thin glass "coverslip" and sealed at the edges to prevent hydrogen ingress. A single LED was used as the light source coupled with two photo detectors. A modulated signal was fed to the LED. The photo detectors were phase locked to the modulated LED signal. The difference in intensity between the "signal" and "reference" photo detectors was measured as a phase shift which is a more sensitive means of detecting small differences in signal strength than directly measuring intensity.
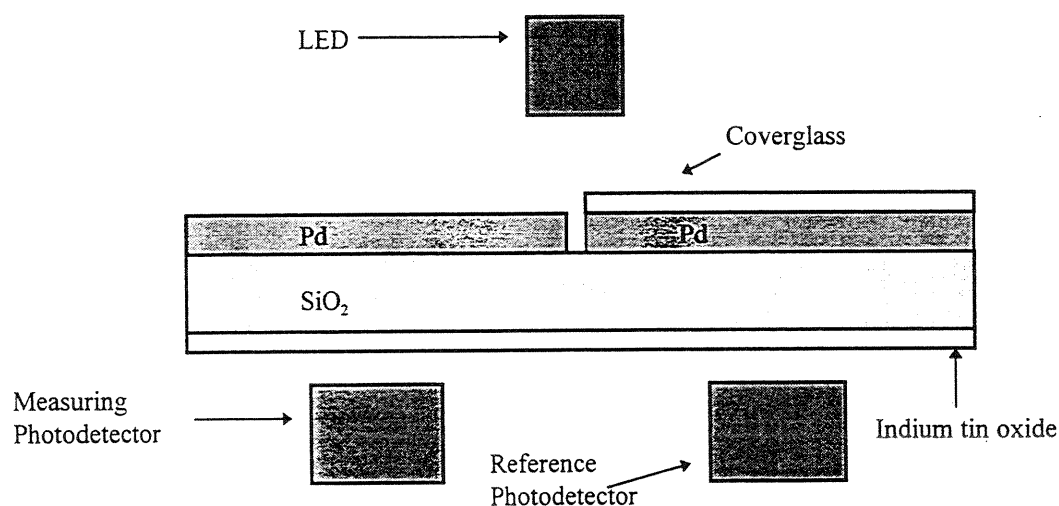

Figure 3. Initial configuration of the hydrogen sensor

Initial tests showed a large and rapid response to the presence of hydrogen. Response (figure 4) was not effected by the presence or absence of oxygen or methane. However water vapour (98% relative humidity at 25°C) slowed response rate and lead to a gradual decline in the response which could be quickly recovered by passing dry gas over the film (5). It was believed that condensation on the film surface was responsible for the observed changes. The fact that both response rate and signal stability were restored by heating the film to about 40°C tends to confirm this hypothesis.
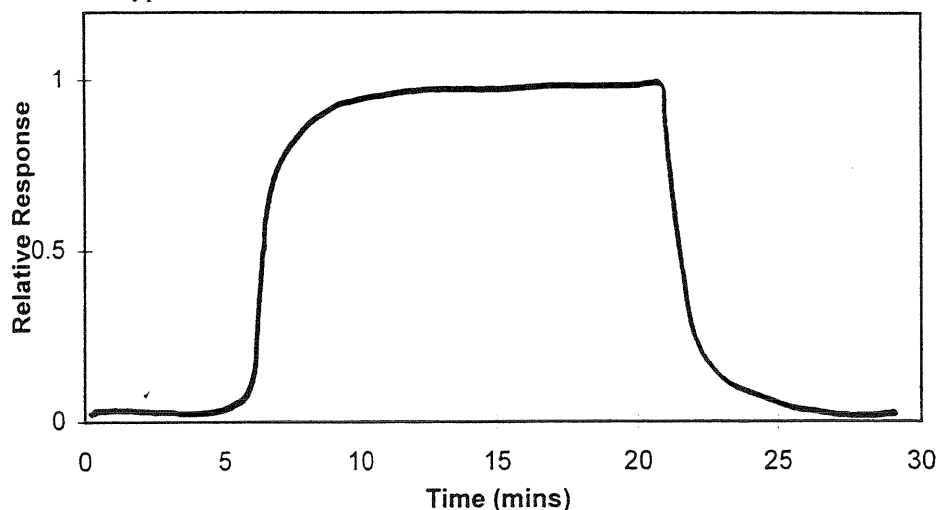

Figure 4. Hydrogen response at 25°C

Interference by carbon monoxide

The detector showed no response to carbon monoxide (6). However when a mixture of carbon monoxide and hydrogen was fed to the detector there was either no response or a very small and slow response to the hydrogen (5). If carbon monoxide was passed over a film containing hydrogen, the hydrogen signal remained steady even when the hydrogen in the gas mixture was removed. Obviously the carbon monoxide was being preferentially absorbed onto the surface of the palladium film and acted as a "blanket" preventing either the entry or exit of the hydrogen.

Of the many attempts to overcome the problem one of the more successful involved the use of a newly developed catalyst (7) capable of selectively oxidising (and therefore removing) carbon monoxide at room temperature in conditions of high humidity. It was found that while the catalyst did remove the bulk of the carbon monoxide, the remaining carbon monoxide built up on the palladium film slowing the sensor response until it became unacceptable.

Pd film Temp (C)	20		50		60		70		80	
Gases	H2	H2:CO	H2	H2:CO	H2	H2:CO	H2	H2:CO	H2	H2:CO
Relative Response	100	-	51	36	44	44	35	35	33	33
Response time (sec)	540	-	660	-	20	480	15	150	10	20

Table 1. Temperature effects on hydrogen response

The carbon monoxide interference was finally eliminated by heating the palladium film (8,9). It was found necessary (Table 1) to heat the film to 70°C to obtain a response whose magnitude was unaltered by the presence of carbon monoxide and whose rate was acceptable (90% complete within 30 seconds). Unfortunately at 70°C the magnitude of the transmission change was only 30% of that at 25°C because the α-β phase transition was no longer occurring at the hydrogen levels (1-4%) being investigated. Although the magnitude of the signal was less (and consequently sensitivity reduced), the signal was quite reproducible and calibration curves were determined (Figure 5). Indium-tin oxide which is both conductive and optically transparent was coated onto the underside of the 7059 glass side to provide resistive heating.

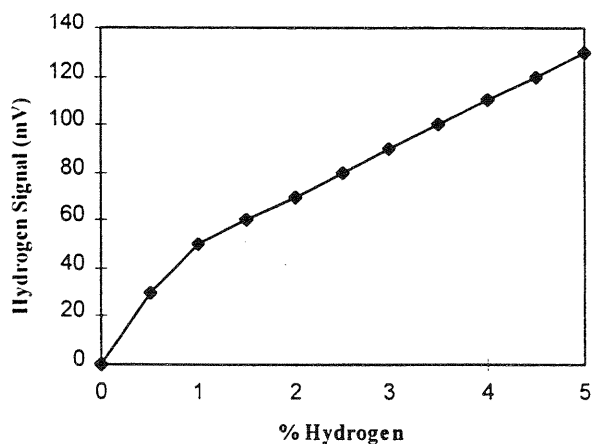**Hydrogen Sensor Calibration Curve**

Figure 5. Calibration curve for the hydrogen sensor.

Poisons

To determine the effect of various poisons, a detector was placed in a test box which had a volume of 5 litres and was fitted with a fan. The box was filled with a gas mixture containing 2% hydrogen and then the various poisons were added.

Sulphur Dioxide: Added 25 ml of 1000ppm SO_2 to the 5 litre box producing a SO_2 level of 5ppm. There was no change of signal. The nose can detect SO_2 at the 3ppm level.

Hydrogen Sulphide: Added 5ml of 1% H_2S to 5 litres producing an H_2S level of 10 ppm which had no effect on detector. The nose can detect H_2S at levels of 1ppm.

Hydraulic Fluid: An evaporating dish containing 100ml of hydraulic fluid was placed in the box and the fan turned on. No change in the hydrogen response was detected over a period of one hour.

Silicone oil: Silicone oil placed on a Petrie dish in the box caused no change in the hydrogen response although spraying "Mr Sheen" into the box caused the signal to first increase and then decrease.

The above tests were designed to simulate the nature and concentrations of poisons likely to be encountered in a coal mine situation. While it is acknowledged that the tests are relatively qualitative in nature, the results indicate that a hydrogen sensor based on a palladium film should be able to function in a coal mine situation without major poisoning problems.

Baseline drift

To be viable, the sensor needed both a reproducible response and a steady baseline. Having overcome the carbon monoxide interference, attention was next focussed on the drifting baseline. Initially the drift was attributed to "the electronics". However when the detector circuit was run in the absence of a palladium film the baseline was quite steady and there was no perceptible drift. Experiments at room temperature found that hydrogen was slowly getting into the reference film despite all efforts to seal the edges. Removal of the reference film gave a better baseline but sensitivity was lost because of the mismatch between the intensity falling on the "signal" and "reference" photo detectors. Several alternate "inactive" (to hydrogen) reference films were evaluated. Carbon was found to be the best reference film in that its transmission did not change on exposure to hydrogen nor after extended periods at 80°C. After eliminating all other sources of drift it was found that there remained a steady upward movement of the baseline when the sensor was operated at 80°C. Moreover when first exposed to hydrogen, there was a "dip" (Figure 6) in the sensor response before the signal moved to its final value. On removal of the hydrogen, the baseline returned to a value well below that at the start of the hydrogen pulse.
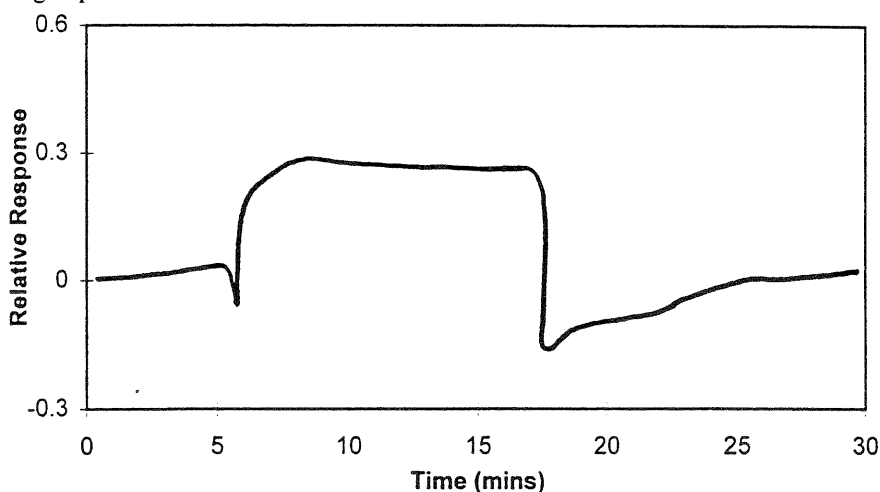

Figure 6. Hydrogen response at 80°C

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To determine the cause of the baseline shift, the film was exposed to hydrogen which was then replaced by nitrogen. The baseline did not drift. Moreover, on repeated hydrogen/nitrogen cycles both the size of the response and the baseline remained unchanged and there was no "dip". On exposure to pure oxygen the baseline rose again, more rapidly than in air. Thus it became obvious that the baseline drift was the result of "oxidation" of the palladium film.

The sequence of events can be explained as follows. All palladium films, whether deposited by R.F. Magnetron sputtering or thermal evaporation are to some extent porous. Oxygen has the ability to diffuse into the pores and dissociate on the walls. After extended exposure to air (oxygen) at 80°C, dissociated oxygen is to be found throughout the film resulting in an increase in its transmission and the upward movement of the baseline. On first exposure to hydrogen, the dissociated oxygen on the surface is reduced by the hydrogen, decreasing film transmission and causing the observed "dip" in the baseline. Continuing or repeated exposures to hydrogen removes oxygen from the pores so that finally there is no drop in the baseline after exposure to hydrogen. The rate of oxygen removal is a function of film deposition conditions and operation temperature.

Gold capping film

It was found that a thin film of gold over the palladium prevented the palladium/oxygen interaction. Unfortunately the gold film decreased the rate of sensor response. Optimisation of the gold film thickness to a value of "one second deposition time" (Table 2) produced a sensor with acceptable response rate (Figure 7). The final sensor configuration is shown in Figure 8.

Film	Relative Response				Response time (sec)			
	70		80		70		80	
	H2	H2:CO	H2	H2:CO	H2	H2:CO	H2	H2:CO
Pd (14) / Au (1)	100	100	95	95	10	25	10	20
Pd (14) / Au (4)	100	100	95	95	10	25	20	30
Pd (14) / Au (8)	110	90	80	60	10	240	-	50
Pd (14) / Au (12)	115	50	-	-	20	150	-	-

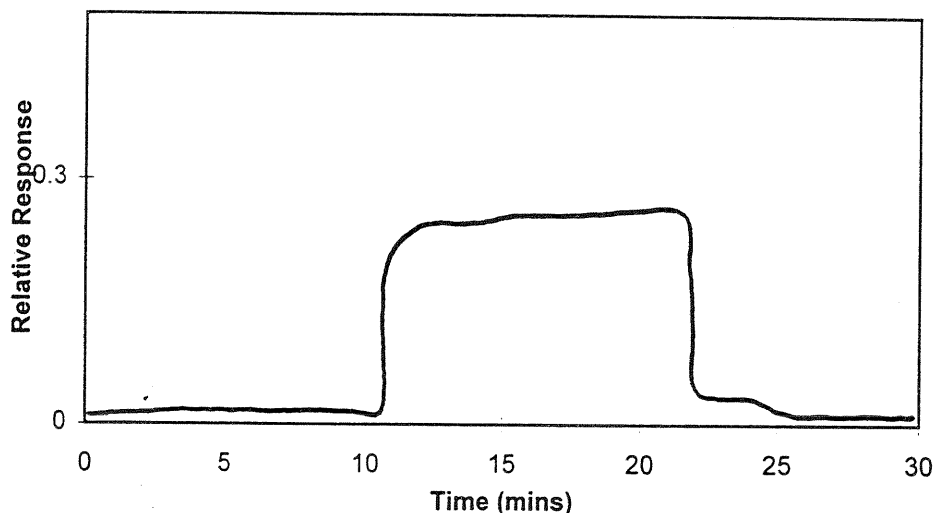Table 2. Effects of increasing gold thickness on hydrogen response

Figure 7. Response of the gold coated sensor.
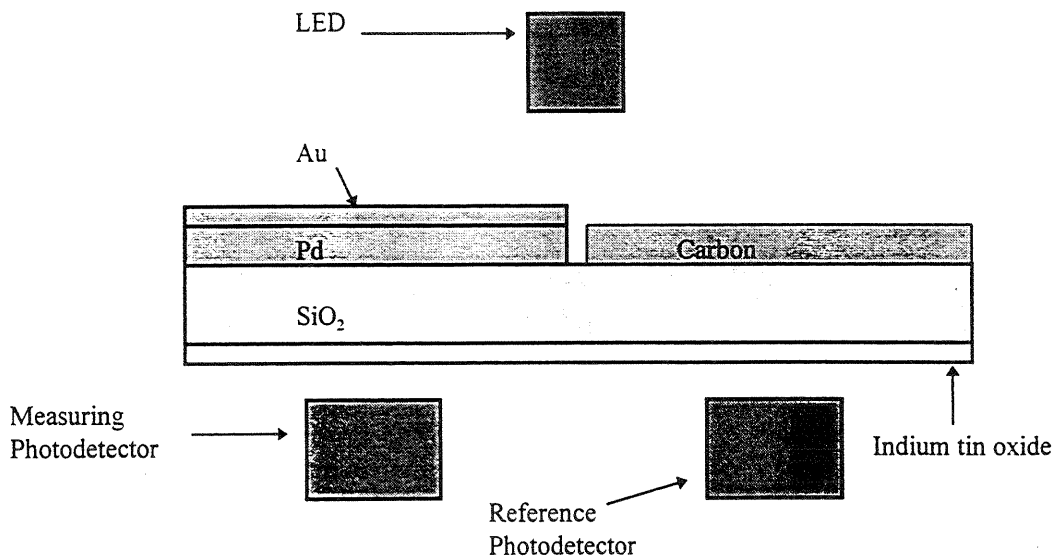
Figure 8. Final hydrogen sensor configuration

It was found that after three or four days at 80°C, the gold coated films began to behave like the plain palladium films, that is, they exhibited baseline drift and a "dip" on first exposure to hydrogen.

X-ray photoelectron Spectroscopy (XPS) depth profiling was used to analyse the very thin gold and palladium coatings. The gold layer on a sample which had not been heated or exposed to hydrogen could be removed in approximately ten seconds (Figure 9) whereas samples which had been heated required approximately 23 seconds for removal of the gold (Figure 10). This indicates that on heating, the gold diffuses into the palladium. Analysis of the palladium indicated that, as would be expected, palladium concentration near to the surface is greater after heating than before. The XPS depth profile results confirmed that, as a result of diffusion, failure of the sensor was the result of the gold layer no longer providing an adequate barrier to prevent the palladium/oxygen interaction.
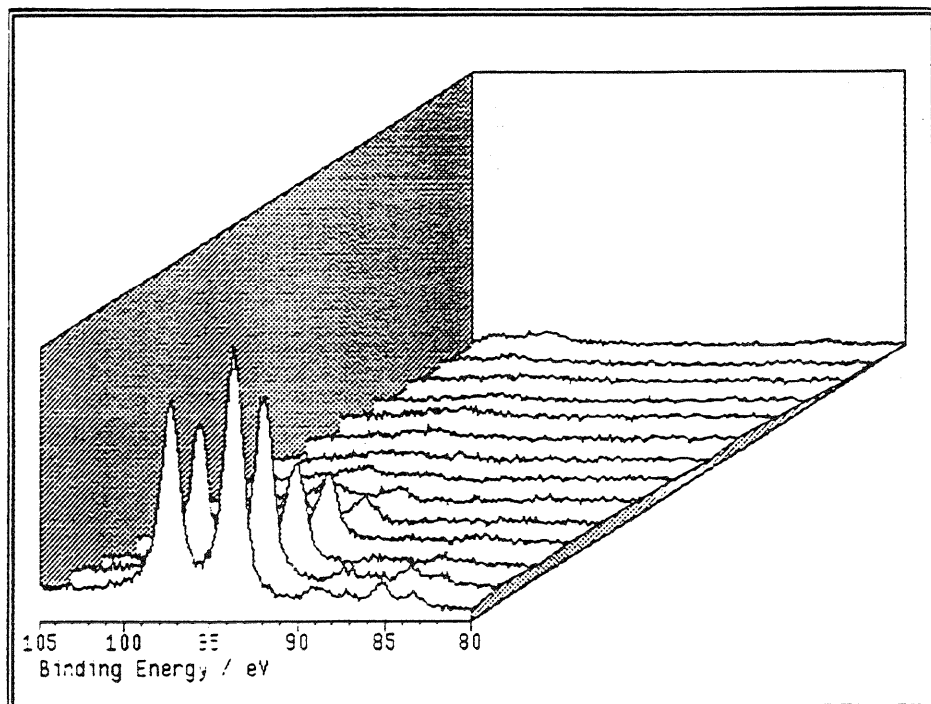

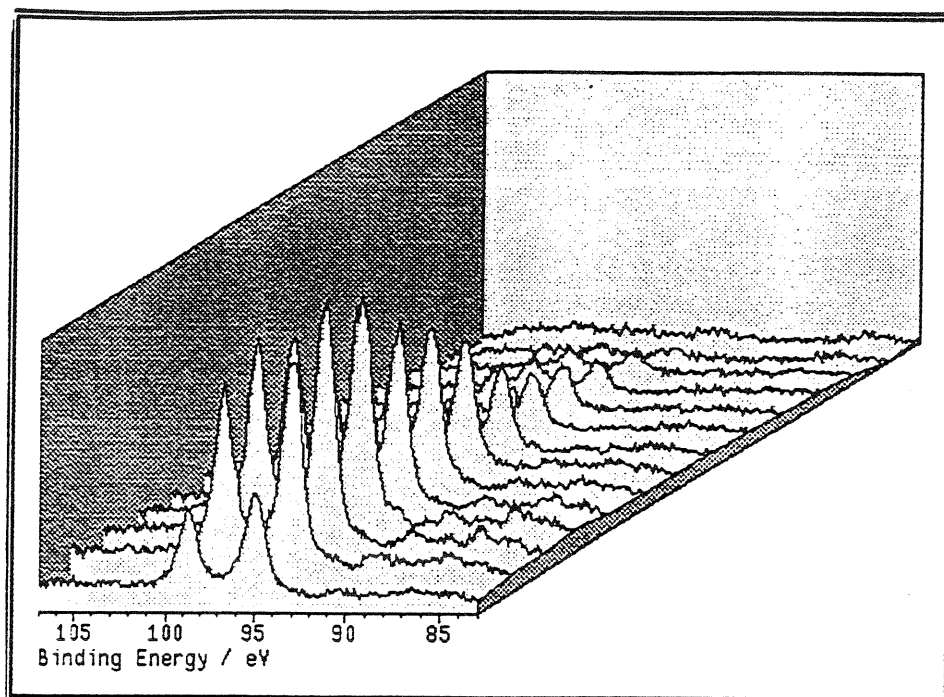Figure 9. Results of the XPS depth profile on unexposed film

Figure 10. Results of the XPS depth profile on exposed film.

Conclusion

A palladium film sensor has been developed which can successfully measure percentage levels of hydrogen in post explosion coal mine atmospheres. Carbon monoxide interference is eliminated by heating the film. "Oxidation" of the palladium is prevented by capping the palladium film with gold. However because of interdiffusion of the gold and palladium at the operational temperatures, the lifetime of the sensor is too short to be of practical value. The final solution appears to require the use of palladium alloys less susceptible to "oxidation" or alternate oxygen barrier layers.

Acknowledgments

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