Methane Formation on H_2 Purification Using a Commercial Pd-Ag Membrane

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Hydrogen is being used in many semiconductor manufacturing steps as a reactant or as a carrier gas. Examples of these process steps are silicon epitaxy, doping of boron, and chemical vapor deposition (CVD) of tungsten metal. In many of these processes, ultrahigh-purity (UHP) hydrogen is required to ensure the desirable properties of the semiconductor product.

UHP H_2 can be generated in different ways. In places where liquid H_2 is readily available, UHP H_2 can be obtained by ''vapor withdrawal'' in that only the vapor phase of the H_2 is taken from a liquid H_2 storage tank. No purifier is needed. Homyak et al. (1995) demonstrated that vapor H_2 gas from a liquid source contained impurities with concentrations well below parts-per-billion (ppb) levels. Presumably, all impurities were trapped in the liquid H_2, since H_2 has the lowest boiling point (except for helium) of all gases. In areas where only pipeline gaseous H_2 is available, such as most of Asia, purification is required to remove impurities such as N_2, O_2, CO, CO_2, CH_4, and H_2O.

One common commercial H_2 purifier uses a Ag-Pd alloy membrane. This precious-metal-based membrane purifies H_2 by a mechanism in which the H_2 transports through the nonporous membrane as protons. After diffusing through the membrane, the protons recombine (with electrons) to form H_2 molecules. This mechanism should exclude impurities from permeating through the membrane. The H_2 permeability of the Ag-Pd membrane increases with increasing temperature. For the membrane to be cost-effective, the operating temperature for the membrane is usually between 350 and 450°C.

Recently, in an effort to qualify a commercial Ag-Pd membrane purifier for a customer in the electronics industry, we discovered that CO and CO_2 in the feed hydrogen can result in traces of CH_4 in the purified product. The formation of CH_4, even in trace levels, disqualifies the product for the customer. This specific customer requires a CH_4 concentration to be less than 10 ppb by volume (ppbv) in hydrogen. For CH_4 to form, carbon has to be present in some form. We hypothesized that CO and CO_2 decomposed to C and O on the membrane surface, and that C diffused across the membrane and then reacted with the product H_2 to form CH_4.

Carbon transportation through a Pd membrane has been reported in the literature. For instance, Ziemecki (1987) demonstrated a catalytic water−gas shift reaction resulting from C diffusion across a Pd membrane. Ethylene was used as the carbon source. Apparently, ethylene decomposed on one side of the membrane to C and H_2, and C diffused through Pd membrane to react with the water vapor on the other side.

This note presents experimental evidence of CH_4 formation from a commercial Ag-Pd membrane on the product side as a result of CO and CO_2 present on the feed side.

Equipment Setup

The experimental setup is shown in Figure 1. The purifier was supplied by Johnson-Matthey using a standard commercial Ag-Pd membrane about 120 μm thick.

The designed flow of this purifier is 14.9 m^3/h (422 std. ft^3/h) at 1,723 kPa (250 psig) inlet pressure and 689 kPa (100 psig) outlet pressure. The purifier has a bleed rate of 2 L/min. Hydrogen was supplied by a bank of Hydril Tubes. Impurities were added using a Challenge Gas Cylinder where impurities were blended.

Analytical Process

Accurate analysis of the feed gas and the product gas was a critical part of the experiment. To analyze the inlet gas, three analyzers were used. A Trace Gas Analyzer Model 4000 made by Valco Instruments was used to measure the concentrations of CO, CO_2, N_2, and CH_4. The Valco analyzer was a gas chromatograph equipped with a helium ionization detector capable of detecting the impurities at the ppbv level (Maroulis and Martinez de Pinillos, 1985). A Meeco Aquamatic Plus analyzer was used to determine the water content. The detectable limit of the Meeco analyzer was around 10 ppbv (Zatko and Ragsdale, 1988). The O_2 level was quantified by an Osaka MK III/Y analyzer with a sensitivity of 2

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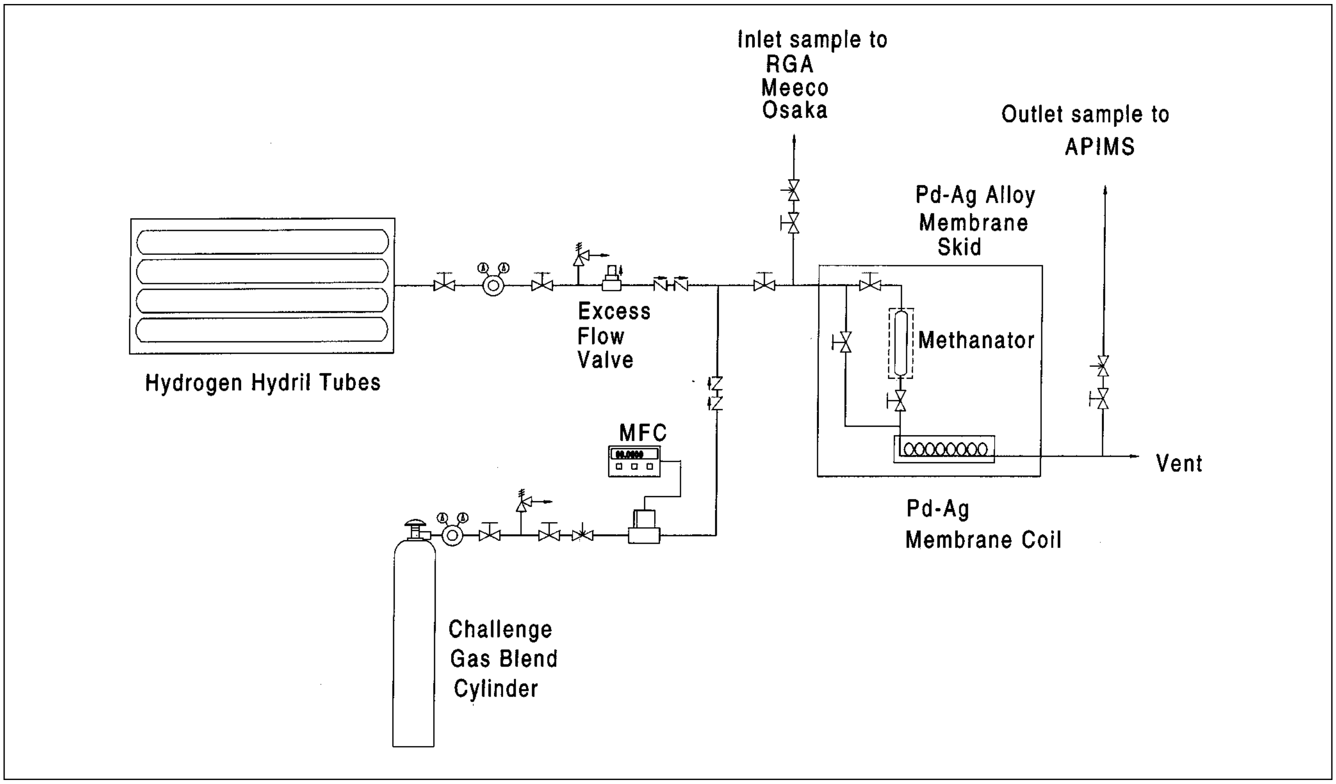

Figure 1. Test apparatus.

ppb by volume. The product stream was continuously monitored by a VG APIX Atmospheric Pressure Ionization Mass Spectrometer (APIMS). APIMS has been shown to be able to detect all these impurities at levels below ppbv in H_2 (Homyak et al., 1995; Sugiyama et al., 1988).

Results

The experimental system was first purged with purified hydrogen until all impurities in the product were below 10 ppbv, analyzed by APIMS. Several experiments were conducted using different challenges.

Challenge with CO, CO_2, and CH_4

The hydrogen was then spiked with 60 parts-per-million by volume (ppmv) of CO, 60 ppmv CO_2, 60 ppmv CH_4, and 1200 ppmv N_2. The purifier temperature was at 350°C. After about 30 min, the impurity challenge was reduced to a more realistic level of 20 ppmv CO, 20 ppmv CO_2, 20 ppmv CH_4, and 400 ppmv N_2. The product stream was continuously monitored by the APIMS during the impurity challenge.

Figure 2 shows the results from the APIMS. While no other impurities were observed in the purified H_2 stream, CH_4 started to elute after about 95 min from when the first challenge was introduced. In an additional 95 min, the CH_4 concentration increased gradually from 4 ppbv to above 10 ppbv, when the challenge was shut off. Methane continued to form for several hours after the termination of the challenge. Water and oxygen in the product, however, remained constant at around 2 ppbv. At the end of the experiment, a temperature increase from 350 to 400°C increased the CH_4 concentration in the product.

Another experiment was conducted with lower impurity concentrations. After the membrane cell was purged at 400°C, the cell temperature was reduced to 350°C and the membrane was challenged with 5 ppmv each of CO, CO_2, CH_4, and 100 ppmv N_2. The APIMS result on the product hydrogen stream is shown in Figure 3.

Approximately 90 min after the challenge, the CH_4 concentration in the product started to climb slowly. The concentration increase continued for more than 10 h, and an equilibrium was not reached. Again, the water and the oxygen concentrations did not increase with the increase of CH_4.

A series of experiments was then performed to identify the source of the CH_4.

Challenge with CH_4 only

"Can CH_4 transport through the membrane?" is an obvious question to ask. To test whether CH_4 could transport through the membrane, we challenged the purifier with hydrogen containing only methane. First, the Pd membrane was purged with purified H_2 at 400°C and then reduced to 375°C. All impurities in the product H_2 were below 10 ppbv before the challenge. We started the challenge with 25 ppmv CH_4, with no other impurities added. The purifier temperature was maintained at 375°C. The CH_4 challenge lasted for more than 6 h. The product H_2 was monitored by the APIMS, and the results are presented in Figure 4.

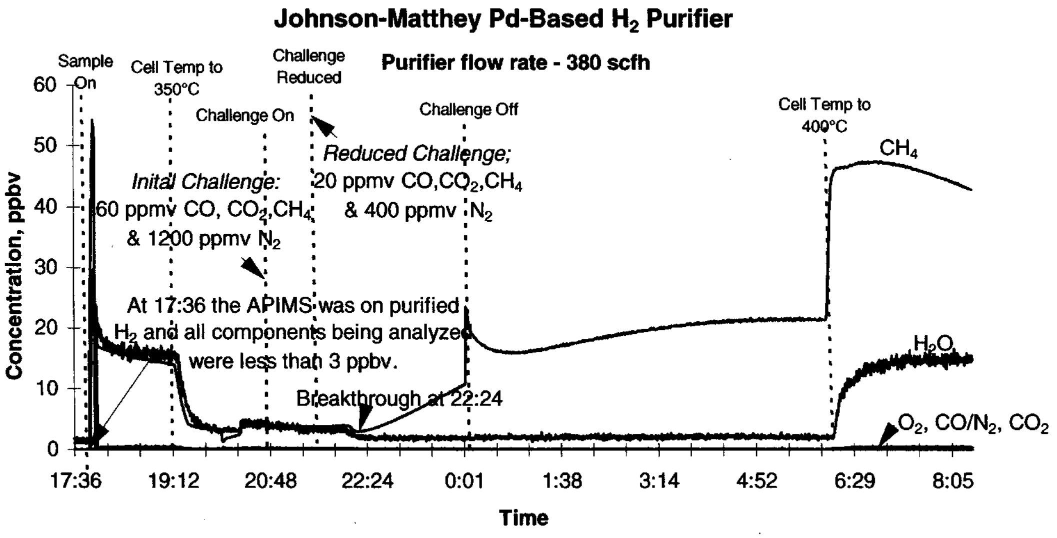

Figure 2. APIMS result on challenge containing CO, CO_2, CH_4, and N_2.

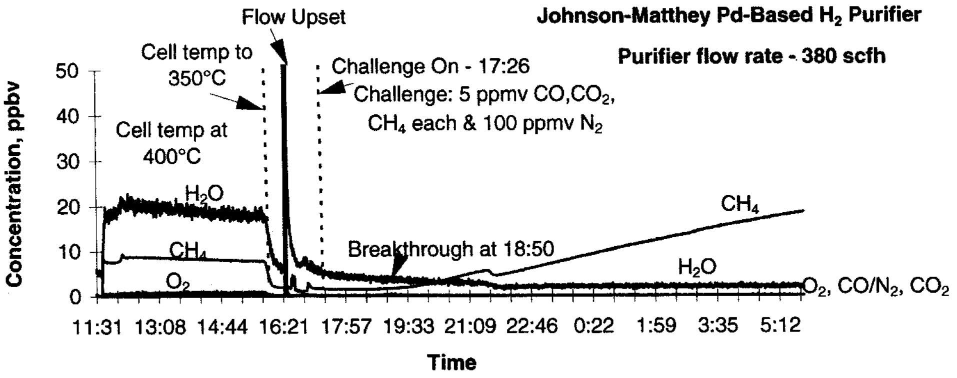

Figure 3. APIMS result on low concentration challenge.

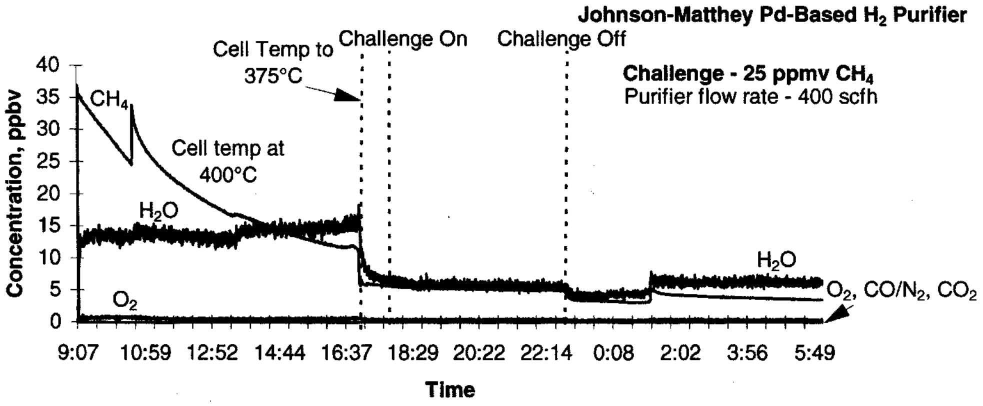

Figure 4. APIMS result on challenge containing only CH_4.

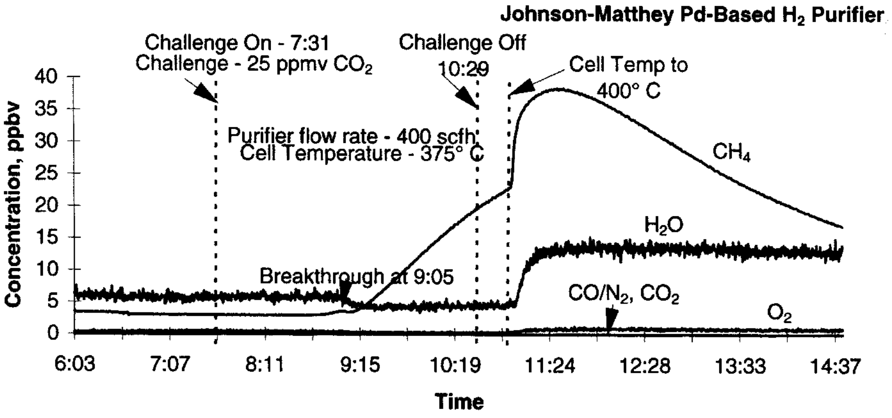

Figure 5. APIMS result on challenge containing only CO_2.

Methane in the H_2 product remained stable and well below the target 10 ppbv level, suggesting that CH_4 in the feed did not affect the purity in the product. There was a drop of CH_4 from 5 ppbv to 4 ppbv over a period of approximately 2 h after the challenge was turned off. No apparent reason can be offered for this phenomenon.

Challenge with CO_2 only

To further investigate the CH_4 formation, we challenged the purifier with only CO_2. After the system was purged to ensure that CH_4 was below 10 ppbv, CO_2 was added to produce a feed concentration of 25 ppmv. The membrane cell was set at 375°C. Figure 5 shows the APIMS data.

About 95 min after the introduction of CO_2, the CH_4 concentration in the product started to increase, while the H_2O and O_2 levels remained stable. In another 85 min, the CH_4 concentration reached 20 ppbv, and the CO_2 challenge was turned off. The CH_4 concentration in the purified H_2 continued to increase. We then raised the cell temperature to 400°C to expedite the cleaning of the membrane. The rate of methane elution increased initially, but it leveled off relatively quickly when the CH_4 concentration reached approximately 38 ppbv. The CH_4 continued to elute for many hours after the CO_2 source was shut off.

Test with methanation catalyst

The preceding experiments suggested that CO_2 and probably CO were the source of CH_4, and that CH_4 in the feed did not contribute to CH_4 in the product. Hence, one logical solution to prevent the CH_4 formation is to convert CO_2 and CO to CH_4 before they pass through the Pd-Ag membrane. An experiment was performed to verify the hypothesis.

The test setup shown in Figure 1 was modified to include a methanation unit installed upstream of the membrane cell. The methanation unit was charged with a commercial methanation catalyst capable of converting CO and CO_2 to CH_4 and H_2O at a temperature of 300°C or higher. The system was challenged with a stream containing CO, CO_2, CH_4, and N_2. The product purity was again monitored by APIMS, and the result is summarized in Figure 6.

The experiment was started with the methanator on-line. After the system was purged to show that all impurities were below 10 ppbv, the purifier was challenged with 350 standard ft^3/h H_2 flow containing 20 ppmv each of CO, CO_2, CH_4, and 400 ppmv N_2. The inlet pressure was at 170 psig and the cell temperature was set at 375°C. For over 3 h, the CH_4 concentration in the product remained constant at a level of approximately 1 ppbv. Some process-variable variations were made, and the responses are shown in the figure. Only small changes (< 2 ppbv) of CH_4 concentration were noted in all process-variable variations.

Discussion

Over a commercial Pd-Ag membrane, the preceding experiments demonstrated the formation of traces of CH_4 when the H_2 feed contained CO_2. Methane, however, does not transport through the membrane. The water and the oxygen concentrations did not increase with the evolution of CH_4, which suggests that O does not transport through the membrane.

In view of data obtained in this study, a plausible mechanism of methane formation in the commercial Pd-Ag alloy membrane might consist of the following steps:

1. Adsorption of CO and CO_2 on the membrane surface;
2. Decomposition of CO and CO_2 on the surface to form C and O;
3. Hydrogen reacts with O to form H_2O;
4. A small portion of the C transport through the membrane via solid phase diffusion;
5. Product H_2 reacts with C to form CH_4;
6. Desorption of CH_4 into product H_2.

The data showed that the CH_4 formation occurred approximately 90 min after the challenge. This slow formation process suggests that Step 4, the solid-phase diffusion, is the rate-determining step. Higher temperatures increased the rate of CH_4 formation.

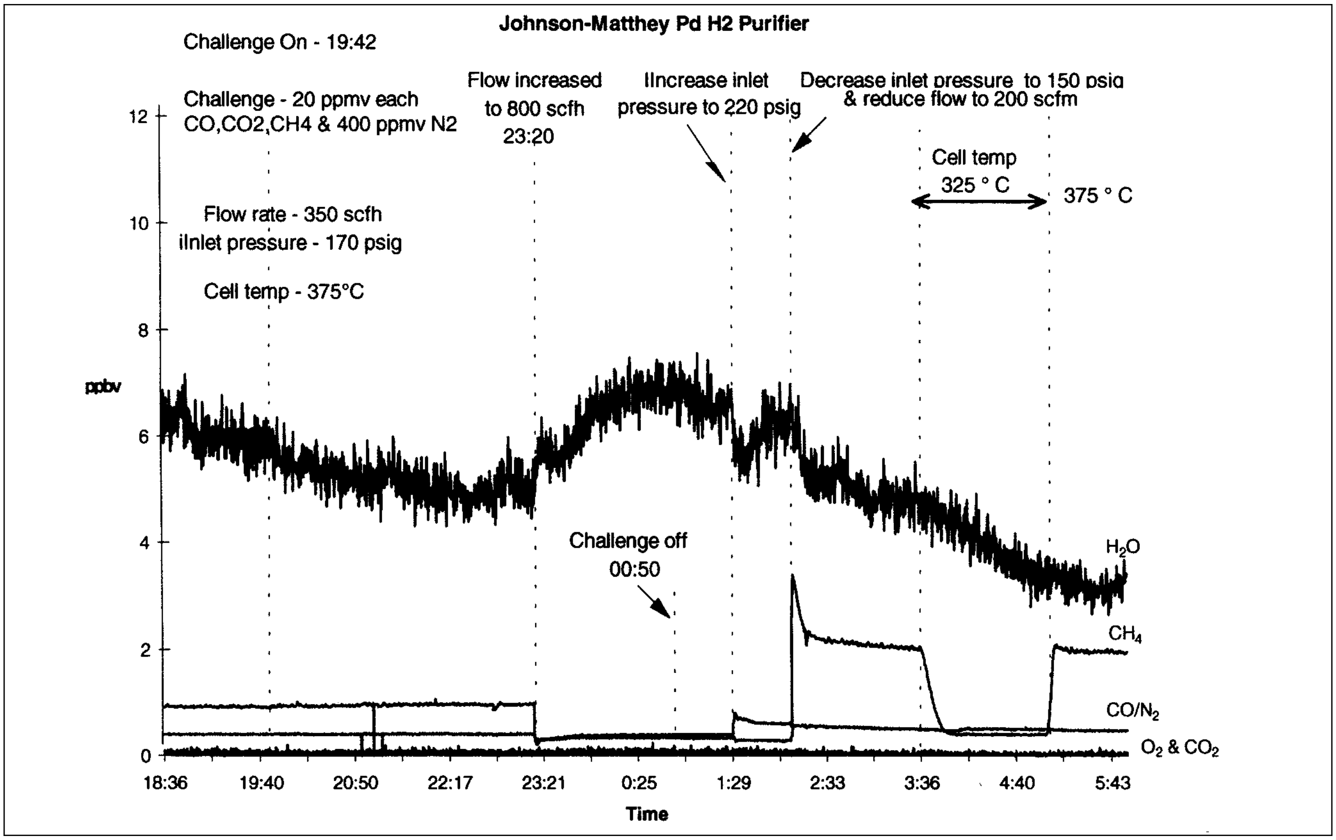

Figure 6. APIMS result with an upstream methanator.

We did not thoroughly study the effects of process variables such as concentration, temperature, and pressure. Additional experiments can be performed to better understand the methane formation.

Conclusion

From the use of highly sensitive analytical equipment, APIMS, we detected trace CH_4 in the product of a commercial Pd-Ag membrane-based hydrogen purifier. Methane formation at ppbv levels was observed when the feed contained ppmv levels of CO and/or CO_2. We hypothesized that CO and CO_2 decomposed on the metal surface to form C, which then transported through the alloy membrane and reacted with the product H_2 to form CH_4. Methane in the feed was stable at the operating temperature range of 350°C to 450°C, and hence was successfully excluded by the membrane.

The problem of methane formation in a Pd-membrane-based purifier can be prevented by installing a methanator before the purifier. The methanator converts the CO and CO_2 in the feed to methane and thereby eliminates the carbon formation. The carbon is believed to be the precursor for the methane in the product.

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