Discussion on hydrogen quality detection methods for polysilicon production

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Abstract. This article analyzed the key factors affecting the quality of hydrogen in combination with the improved Siemens polysilicon production process, and the quality detection methods of hydrogen are discussed. Regarding the different hydrogen sources, more scientific and effective quality detection methods are proposed. It is of great significance to strengthen the quality control of polysilicon production and enhance product competitiveness.

1. Introduction

The improved Siemens method is a mainstream technology for polysilicon production due to its mature technology, stable process, closed loop and low system risk. As one of the important raw materials, hydrogen has a large amount of circulation and high quality requirements. Nowadays, pure hydrogen is produced by electrolytic method for polysilicon production in most of the polysilicon manufacturers. The hydrogen in the tail gas of the reduction furnace and the hydrogen of the system are returned to the production system for cyclic utilization by the dry recovery process and the hydrogen pressure swing adsorption process [1-4]. The content of O₂, N₂, CO, CO₂ and CH₄ in the recovered hydrogen has a different degree of increase than the pure hydrogen. When the efficiency of the activated carbon absorber in the dry recovery process decreases, a small amount of HCl, SiH₂Cl₂, SiHCl₃ and SiCl₄ appears in the dry recovered hydrogen. Besides, elements such as B, Al, P, As, Fe and Cr will be detected in the dry recovered hydrogen. The presence of these impurity components greatly decreased the quality of polysilicon products [5].

In this paper, the composition of impurity components in hydrogen from different sources gathering from the actual production is analyzed and monitored with scientific and effective detection methods. Through the monitoring, the quality of hydrogen can be more comprehensively evaluated, which will help to get the real-time, accurate data for system operation and adjusting the system to maximize production efficiency.
2. Components detection of O₂, N₂, CO, CO₂, CH₄ in the recovered hydrogen

2.1. Thermal conductivity cell gas chromatography (TCD)
Figure 1 shows the schematic diagram of the working principle of the thermal conductivity detector (TCD). TCD is a general-purpose detector responding to the difference in thermal conductivity of the component being tested and the carrier gas. The sample is injected into the chromatograph from the inlet, separated by the column and then the components flow out of the column into the measuring cell. Since the mixture gas has different thermal conductivity from that of the pure carrier gas, which leads to the heat conducted from the hot wire to the cell wall is different, the temperature of the hot wire of the two cells should be different consequently, and further the resistance values of the hot wires of the two cells are different, which cause the balance of the bridge is broken. There is a potential difference between M and N points and output the signal [6].

Figure 1. Schematic diagram of the working principle of the TCD (1. Reference cell; 2. Inlet; 3. Column; 4. Measuring cell)

Figure 2 shows the designed test scheme according to the detected target. TCD detector is applied to quickly detect the O₂, N₂, CO, CH₄ and CO₂ in hydrogen with a detection limit of 5 μL/L, which is suitable for the detection of components in dry recovered hydrogen. However, the content of each component in pure hydrogen is less than 1 μL/L, therefore pure hydrogen cannot be detected using this scheme.

Figure 2. The designed test scheme (1. Injection six-way valve; 2. Inlet; 3. Switch six-way valve; 4/5. Column; 6. TCD)

2.2. Flame ionization detector (FID)
Flame ionization detector (FID) is a selective detector that applies hydrogen flame as the ionization source to ionize organic matter and generate micro-current. It can respond to almost all organic matter [7]. Figure 3 is the schematic drawing of the FID. Since FID only responds to organic compounds, it can only detect CO, CH₄ and CO₂ components in hydrogen, O₂ and N₂ can’t be detected. The scheme for detecting CO, CH₄ and CO₂ components is shown in figure 4.
Figure 3. Schematic diagram of FID detector structure: 1. Capillary column; 2. Nozzle; 3. Hydrogen inlet; 4. Tail gas inlet; 5. Ignition filament; 6. Air inlet; 7. Polarization pole; 8. Collector
This scheme can detect CO, CH$_4$ and CO$_2$ in hydrogen with a detection limit of 0.5 μL/L quickly and accurately. The methane reforming furnace is placed in front of the column and the total content of CO, CH$_4$ and CO$_2$ (naming the total carbon content) is measured. The methane reforming furnace is placed behind the column, the contents of CO, CH$_4$ and CO$_2$ are measured respectively.

Figure 4. The scheme for detecting CO, CH$_4$ and CO$_2$ components 1. Injection six-way valve; 2. Vaporizer; 3. Methane reformer; 4. Column; 5. FID

2.3. Helium discharge ionization detector (DID)
The Helium discharge ionization detector (DID) is a versatile detector with precision of ng/g level. It can also respond to other inorganic and organic compounds beside of neon and is a non-destructive concentration detector [8,9]. Figure 5 is a schematic diagram of the operation of the DID detector.

Figure 5. Schematic diagram of the working principle of the DID
The gas path is designed the same as the TCD detector, which can be applied to detect the O$_2$, N$_2$, CO, CH$_4$ and CO$_2$ components separately in the hydrogen gas. The detecting scheme for DID is shown as figure 6.
DID can achieve high sensitivity and detection limit up to 10ng/g level by using ultra-high purity helium carrier gas, low-loss chromatographic column and good air tightness of the system, which is suitable for the detection of high purity gas components such as pure hydrogen.

3. Components detection of HCl, SiH$_2$Cl$_2$, SiHCl$_3$ and SiCl$_4$ in hydrogen

There are about 80% of H$_2$ is purified by the dry recovery process and returned to the production system for reuse in the improved Siemens polysilicon production process. Once the efficiency of the dry recovery system is reduced, the recovery of H$_2$ will contain HCl, SiH$_2$Cl$_2$, SiHCl$_3$, and SiCl$_4$ components and lead to polysilicon products decline in quality.

According to the principle that the response coefficient of one substance remains unchanged in the TCD detector under the same analysis conditions, the detection method of HCl, SiH$_2$Cl$_2$, SiHCl$_3$ and SiCl$_4$ in H$_2$ is established on the basis of experiment in this paper. Firstly, the response coefficient $f$ of HCl, SiH$_2$Cl$_2$, SiHCl$_3$ and SiCl$_4$ is calculated referring to the standard sample. The gas being tested is carried into the gas chromatograph through the quantitative loop by the carrier gas. The mixture of HCl, SiH$_2$Cl$_2$, SiHCl$_3$ and SiCl$_4$ in the gas is detected by the detector in turn and the peak area of each component is obtained by a data processing system after being separated by the chromatographic column. Finally, the content of each chlorosilane component in the sample gas per unit volume can be calculated according to the response coefficient and the injection volume. The calculation formula is as follows:

$$W_i = \frac{f_i \times A_i}{V}$$

Where: $W_i$ - Content of chlorosilane component, μg/mL; $f_i$ - Response coefficient; $A_i$ - Peak area of the chlorosilane component; $V$ - Quantitative loop volume, mL.

Figure 7 shows the detection scheme of HCl, SiH$_2$Cl$_2$, SiHCl$_3$ and SiCl$_4$ in H$_2$. By detecting the chlorosilane components in the recovered hydrogen, the operating efficiency of the dry recovery system can be monitored, which provides an effective means for production operation and quality control.

4. Detection of impurities of B, Al, P, As and Fe in hydrogen

Acceptor impurities such as B, Al and donor impurities such as P, As are important factors affecting the quality of polysilicon products. Metal impurity elements such as Fe, Cr, Ni, and Cu form deep-level recombination centers which affects the lifetime of minority carriers and reduces the efficiency of solar
cells consequently. The B, P and metal impurity elements in Trichlorosilane can be removed by efficient purification, however, the determination of elemental impurities in hydrogen has few reports. This paper developed a set of trapping devices for elemental impurities in gas shown in figure 8. A certain concentration and volume of ultra-high purity nitric acid is used as the absorption liquid, through adjusting the pressure and flow rate of the sample gas, introducing a certain volume of sample gas, collecting the impurity elements in the sample gas by the absorption liquid, and detecting the absorption by inductively coupled plasma mass spectrometry. And then the content of impurity elements in the liquid can be converted according to the volume of the collected gas to obtain the content of impurity elements in the sample gas [10, 11].

**Figure 8.** Schematic diagram of gas absorption device connection 1. Gas source valve; 2. Pressure regulating valve; 3. Flow meter; 4. Gas cylinder; 5. Wet gas flow meter

### 4.1. Determination of the collecting conditions of impurity elements

The type of absorbent acid, the concentration of absorbent solution and the flow rate of sample gas all affect the collection efficiency of impurity elements in the gas. The optimum conditions of acid composition, absorbent concentration and gas flow velocity are determined by orthogonal test, and the orthogonal test schemes are shown in Tab.1. According to the test results, the optimal condition is No.5, namely, the HNO₃ with a concentration of 5% as the absorption acid, and the flow rate of collected gas is controlled at 120mL/min.

| No. | Acid  | Concentration (%) | Flow rate (mL/min) |
|-----|-------|------------------|-------------------|
| 1   | HCl   | 2                | 40                |
| 2   | HCl   | 5                | 120               |
| 3   | HCl   | 8                | 80                |
| 4   | HNO₃  | 2                | 40                |
| 5   | HNO₃  | 5                | 120               |
| 6   | HNO₃  | 8                | 80                |

### 4.2. Calculation results

The content of impurities in the sample is calculated according to Formula 2. Gas sample is collected under the test conditions, and the content of impurities in the absorbent with the volume of 50mL is detected by ICP-MS.

\[
C_i = \frac{m_i \times 50}{V} \tag{2}
\]

Where: \( C_i \): Element content in gas, ng/m³; \( V \): Volume of the gas sample, m³; \( m_i \): Mass concentration of elements in absorption solution, ng/g.

The content of impurities in hydrogen can be comparatively analyzed by this method. Due to the impurity content in hydrogen is in the level of between \(10^{-12}\) and \(10^{-9}\), the most important of quality control is to prevent contamination. Therefore, the connecting pipelines and absorption bottles must be made of anti-corrosion, and high-purity materials such as PFA or FEP, and should be cleaned and sealed storage to prevent contamination before using.
5. Conclusion
In this paper, several detection methods are discussed according to the different sources of hydrogen in the Siemens polysilicon production process and the quality control elements. A method for detecting the content of chlorosilane in hydrogen is established on the basis of the method and principle of liquid chlorosilane detection. The method for detecting impurities in hydrogen has perfected the quality control system and technical specification of hydrogen, which will be beneficial for the production process control of electronic grade polysilicon products.

With the increasingly high quality requirements for polysilicon products, it is necessary to continuously improve the quality detection technology through developing lower detection limit, more rapid and accurate analytical methods to guarantee the polysilicon production operation.

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