Polysilizium geht online: Der Einsatz von Prozess-Gaschromatographen in der Polysilizium-Produktion

GDCh Arbeitskreis Prozessanalytik
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Outline

1. Polysilicon Manufacturing
2. Examples: Purity Control & Process Control
3. Manufacturing Challenges
4. Value Propositions for Online Analytics
5. Analytical Challenges
6. Conclusion
Polysilicon Manufacturing

Sand, quartz (SiO2) → Polysilicon → Silicon ingot → Silicon wafer → Solar cell

- Silicon (MG-Si)
- Polysilicon
- Solar module
What is Polysilicon?

- Silicon (Si) is a semi-metal and has semiconducting properties
- Polysilicon is highly purified, polycrystalline silicon

**Elemental silicon of different purity:**

- Metallurgical Grade Silicon (MG-Si)
  98 - 99 %
- Solar Grade Silicon (SoG-Si)
  99.9999 - 99.999999 % (6N - 8N)
  Boron (B) < 3 ppm, Phosphorus (P) < 10 ppm, total metallic impurities < 300 ppm (preferably < 150 ppm)
- Electronic Grade Silicon (EG-Si)
  99.9999999 - 99.999999999 % (9N - 11N)
Process Flow Diagram

MG - Si → HSiCl3 production → Siemens reactor → Poly - Si

MG - Si → HCl

HCl → Tank farm → HSiCl3 distillation → Converter

Siemens reactor → Vent gas recovery

H2SiCl2

Cl2

H2
The Siemens Process: Chemical Vapor Deposition

- **Feed gases**
  - Trichlorosilane \( \text{HSiCl}_3 \)
  - Hydrogen \( \text{H}_2 \)
- **Decomposition of \( \text{HSiCl}_3 \) at \( \sim 1000 \, ^\circ\text{C} \):**
  \[
  4 \text{HSiCl}_3 \rightarrow \text{Si} + 3 \text{SiCl}_4 + 2 \text{H}_2
  \]
- **Deposition of the Si-atoms on hot polysilicon slim rods**
- **Final rod diameter \( \sim 200 \, \text{mm} \)**
- **Recovery and recycling of by-products**
Siemens Reactor: Charging

5 Days
Process Control & Process Optimization: e.g. Siemens Reactor

Feed gas regulation

Feed gas
TCS + H₂

Vent gas

VGR unit

Reactor efficiency
VGR operation
Polysilicon Manufacturing: Challenges (I)

- Chemicals:
  - Highly flammable & explosive
  - Highly corrosive
  - Toxic
  - Air and moisture sensitive (forming HCl & SiO₂)
  - Violent reaction with water
- Manufacturing process is extremely energy consuming
- Low product yields (CVD reactor & converter)
- High turnover of materials (recycling)
- Stable product quality is crucial
- Products are extremely precious
- High degree of operational know-how required
- Very limited availability of experienced process engineers
- Operator companies very concerned about intellectual property

Trichlorosilane (TCS), HSiCl₃:
Polysilicon Manufacturing: Challenges (II)

Cost pressure on polysilicon production is rapidly raising:

- Solar energy costs have to drop to be competitive in the future energy mix
  - Target spot price of 35 $US / kg polysilicon
- Many newcomers are entering the solar business worldwide:
  - Lower energy costs in Asia
  - Lower labor costs in Asia
  - Environmental regulations less stringent
  - Health protection less stringent
- Established manufactures ramp up their polysilicon capacities to flood the market
  - Strategy to protect against newcomers to the market
- Innovative technologies are outpacing the traditional Siemens process:
  - Enhancement of the Siemens process
  - SiH₄ based technologies - less energy consuming
  - FBR - continuous process, no chlorine chemistry, simplified vent gas recovery, low energy
  - Metallurgical upgrading - more economic but 5N only
Polysilicon Manufacturing: Challenges (III)

Across the COMPLETE production chain

Online GC addresses all three issues
Value Propositions for Online Analytics

- Shortening of time to market (first silicon out)
  Fast ramp-up and stable operation of CVD reactors
- Increase of polysilicon output
- Reduction of production costs
  Less feed gas consumption, heating & cooling, vent gas treatment, waste products
- Enhancement of polysilicon quality
  Permanent control of the feed gas purity
- Total product traceability along the complete value chain
- Ensures process safety (personnel & plant)
- Reliability of analysis results
- Comprehensive knowledge based on sufficient process data
Analytical Challenges

- Expertise in chromatographic separation of uncommon components
- Ability to handle highly reactive samples in the application laboratory
- Customer samples are not available for method development
- Commercial availability of calibration blends is very limited
- Shipping of calibration blends is cumbersome & expensive
- Special sample pre-treatment to remove low-volatiles (AlCl3, polysilanechlorides)
- Highly leak-proof design of sample conditioning systems
  Special fitting techniques, seals & hardware components
- Special layout of SCS to allow for purging procedures
- Special concept for SCS to minimize sample consumption
- Effective protection against corrosion
- Proper selection of analytical hardware (valves, columns etc.)
- Trace level detection at ppb levels
- Sample condensation
Conclusion

Polysilicon manufacturing:

- GC systems have been installed and commissioned in many polysilicon plants worldwide and are operating to the full satisfaction of customers
- Process GCs are increasingly replacing offline GCs
- The use of online analytics is becoming an accepted standard
- Online analytics is playing a significant role in establishing solar energy in the future energy mix

Generally:

- Expertise of Siemens Process Analytics in sophisticated chemical applications pays off
- Emerging markets and technologies offer new opportunities for established analyzer techniques
Thank you for your attention!

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