The preparation and detection of high purity silicon tetrachloride with optical fibres level

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Abstract
This article showed a technology for producing high purity silicon tetrachloride with optical fiber level, which using the method of adsorption unite distillation, whose material belong to by-product of polysilicon system. This technology could remove chlorosilane, metal impurities and impurities containing hydrogen effectively. Test’s results showed that most indexes can meet or exceed the standards of Evonic, indicating that product produced by this technology can meet the demand of processing optical fiber preforms what is OVD level completely. This technology has the advantages of simple process, continuous operation, and large capacity and so on, and industrialization can be realized.

1. Introduction
Today, Modified Siemens Process has already been one main process for producing polysilicon, however, it can also generate too much SiCl₄ in the manufacturing process. For example, if one company produced 10000t polysilicon, it would also produce 200000t SiCl₄ [1]. How to recycle SiCl₄ has been one key for influencing development of polysilicon company. Most polysilicon companies usually recycle SiCl₄ into process system to produce trichlorosilane, adopting the method of cold hydrogenation. With the forward study of SiCl₄, it has found that SiCl₄ can also be used for manufacturing many high value-added silica-based materials, such as fumed silica, optical fiber perform, ethyl silicate [2, 3, and 4].

High purity SiCl₄ is an important material for manufacturing optical fiber performs, having been one indispensable materials for optical communication industry. However, being limited by domestic purification technology, 80-90% SiCl₄ for optical fiber has to import [5]. So, this article designed one purification technology for manufacturing high purity SiCl₄ using co-product SiCl₄ from polysilicon company. Test’s results showed that index did reach the international advanced level.

2. Experiment

2.1. Preparing high purity SiCl₄
Firstly, technology took impure SiCl₄ into crude distillation column (stainless steel) to remove low and high boiling substances continuously. Low purity SiCl₄ went into 1# tower to remove low boiling substances, such as trichlorosilane and dichlorosilane. Those low boiling substances went out through...
tower top, and intermediate product located at tower bottom would go into 2#tower to remove high boiling substances containing B, P elements in SiCl₄. At the top of 2#tower, the mass fraction of SiCl₄ would be not lower than 99.99%. Then, technology made use of adsorption column (stainless steel) to remove impurities containing hydrogen in system. After that, intermediate product went into distillation column to remove low and high boiling substances again, and prepared ultrapure SiCl₄ in the end. The preparing process was shown in Fig. 1.

At the section of crude distillation, it need to pump high purity N₂ into crude distillation column. By controlling temperature, the low and high boiling substances could be transferred with a certain proportion, the temperature of column bottom should be controlled at 75-80°C, of tower top should be controlled at 65-70°C. At the phase of absorption, it made use of globular activated carbon as adsorbent to remove metal impurities and impurities containing hydrogen, adsorbent temperature should be controlled at 20-40°C.

At the phase of distillation, SiCl₄ after adsorbed was transported into effective distillation column, at the protection of high pure N₂. Like crude distillation, low and high boiling substances should be removed with one certain proportion through controlling temperature, temperature at column bottom should be controlled at 75-80°C, at tower top should be controlled at 65-70°C, and the reflux ratio should be not less than 10:1.

2.2. Analysis and Determination
Using G-C (7890A, Agilent) tested the content of chlorosilane impurities in SiCl₄ prepared by this technology; using ICP-MS (7700, Agilent) tested the content of metals impurities; using FT-IR (Is5, Thermos Fisher) tested the content of impurities with hydrogen. Technology also designed one online sampling system, which can sample and test online to realize the isolation between detecting system and surrounding, guaranteeing veracity of test results.

3. Results and Discussion
3.1. Coarse Rectifying
Fig. 2 was results of component test of crude SiCl₄ before or after coarse distillation, particular dates were showed in Table 1. It could found that SiHCl₃ was wiped off effectively, after coarse distillation.
Table 1. The component of impure SiCl4.

| component                  | SiCl4 (%) | SiHCl3 (%) | SiH2Cl2 (%) |
|----------------------------|-----------|------------|-------------|
| impure SiCl4              | 98.5      | 1.5        | 0           |
| after coarse distillation  | >99.99    | <0.01      | 0           |

Table 2. Content of metal impurities before and after adsorption (ng·g⁻¹).

| sample | Al  | Fe  | Cu  | Cr  | Mn  | Ni  | V   | Co  | Zn  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| before | 12.32 | 27.69 | 0.10 | 3.83 | 0.14 | 0.06 | 0.05 | 0.20 |
| after  | 1.25 | 2.46 | 0.05 | 0.74 | 0.09 | 0.11 | 0.05 | 0.01 | 0.06 |

3.2. Absorbing
Table 2 was the test of metal impurities in SiCl4 before and after adsorption, results showed that each metal impurity was dropped sharply after adsorption.

3.3. Rectificating
Fig. 3(a) was FT-TR of impurities contain hydrogen in SiCl4 before distillation. Results showed that the infrared transmittance of main compounds impurities contain hydrogen were still low, after being rough distillated and adsorbed, although the content of metal impurities has already as low as 5 ppb.
Figure 3. The infrared transmittance of hydrogen compounds in SiCl4 before and after distillation.

Fig. 3(b) was FT-TR of SiCl4 after distillation, it can be found that infrared transmittance of compounds contain hydrogen increased generally at 3045 cm\(^{-1}\), 2338 cm\(^{-1}\), 2295 cm\(^{-1}\), even some perssad were up to 99\%, after further distillation.

Distillation is the method which is used most widely to separate liquid mixtures. It has advantages of simple operation, automation, continuous production, large output and so on. It has already been used to manufacture high purity SiCl4 for optical fiber\(^{[7, 8]}\). Experiment proved that distillation can remove hydrogen compounds effectively, if the distillation flow and parameters can get reasonable layout.

3.4. Quality Comparing

Table 3 was a comparison about content of metal impurities in SiCl4 between this technology and YFOC or Evonic. Results showed that metal impurities’ content in SiCl4 prepared by this technology were all lower than YFOC, main metal impurities was inferior to Evonic. But the control for Al, Fe and Cr was not so better, it perhaps because that impure SiCl4 used in this technology comes from polysilicon system, and those impurities mainly came from industrial Si. Meanwhile, Stainless Steel tube were used totally in technology system as pipeline welding and installation, unsmooth surface could cause chemical micro-pollution, which could improve the content of Cr in product. This problem can be dealt with the method of polishing treatment\(^{[9]}\).

| Sample | Al (ng·g\(^{-1}\)) | Fe (ng·g\(^{-1}\)) | Cu (ng·g\(^{-1}\)) | Cr (ng·g\(^{-1}\)) | Mn (ng·g\(^{-1}\)) | Ni (ng·g\(^{-1}\)) | V (ng·g\(^{-1}\)) | Co (ng·g\(^{-1}\)) | Zn (ng·g\(^{-1}\)) |
|--------|------------------|------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| YFOC   | 1.00             | 3.00             | 1.00             | 1.00            | 0.50            | 1.00            | 1.00            | 1.00            | 1.00            |
| Evonic | 0.50             | 1.50             | 0.25             | 0.50            | 0.50            | 0.50            | 0.50            | 0.50            | 0.50            |
| Sample | 0.85             | 2.46             | 0.05             | 0.74            | 0.09            | 0.11            | 0.05            | 0.01            | 0.06            |

Table 4 was the comparison about content of impurities containing hydrogen in SiCl4 prepared by this technology and standard of Evonic. It could be found that the infrared transmittance of other hydrogen compounds impurities except Si (CH\(_3\)) Cl\(_3\) both meet the standard of Evonic. This is for that Si (CH\(_3\)) Cl\(_3\) can form one azeotrope with SiCl4, because of their nearly same boiling point; and it need too much plate number and reflux ratio to wipe off, which is a limit for the use of distillation operation for preparing very pure SiCl4 with optical fiber level. For Si (CH\(_3\)) Cl\(_3\) impurities, it can be removed through photo chlorination or low temperature plasma method.
Table 4. Content of hydrogen compounds compares with the standard of Evonic.

| hydrogen compounds | wavelength       | standard of Evonic | sample   |
|--------------------|------------------|--------------------|----------|
| Si(OH)Cl3          | 3666 cm⁻¹        | ≥90%               | 99.36%   |
| -CH                | 3100-3020 cm⁻¹   | ≥99%               | 99.75%   |
| -CH                | 2970-2925 cm⁻¹   | ≥95%               | 99.70%   |
| HCl                | 2860-2830 cm⁻¹   | ≥95%               | 99.86%   |
| CO₂                | 2338 cm⁻¹        | ≥95%               | 99.29%   |
| Si(NCO)₄           | 2295 cm⁻¹        | ≥97%               | 100.00%  |
| SiHCl₃             | 2257 cm⁻¹        | ≥99%               | 100.00%  |
| Si(CH₃)Cl₃         | 2023 cm⁻¹        | ≥99%               | 97.93%   |
| Si₂OCl₆            | 1540 cm⁻¹        | ≥99%               | 99.49%   |

4. Conclusion
This study prepared high purity SiCl₄ with the method of distillation unite adsorption, results showed that contents of main metals and hydrogen compounds impurities are better than the standard of Evonic, which can meet the demand of optical fiber perform with OVD grade.

Comparing with Evonic, metal impurity containing Al and Fe are a little higher. It indicates that company should control the quality of raw material strictly, and remove it through distillation as far as possible, before starting to produce very pure SiCl₄. For higher content of Cr, it should handle with the pipeline selection and welding technology.

It is too hard to remove Si (CH₃) Cl₃ with traditional distillation technology for its nearly same boiling points with SiCl₄. But, it still can improve the quality of products further through the method of photo chlorination for removing Si (CH₃) Cl₃, which can meet the requirement for optical fiber performs with PCVD grade.

The technology has the advantages of simple process, continuous operation, and large capacity and so on. It can realize industrialization, and make a good foundation for the localization of SiCl₄ with optical fiber grade.

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