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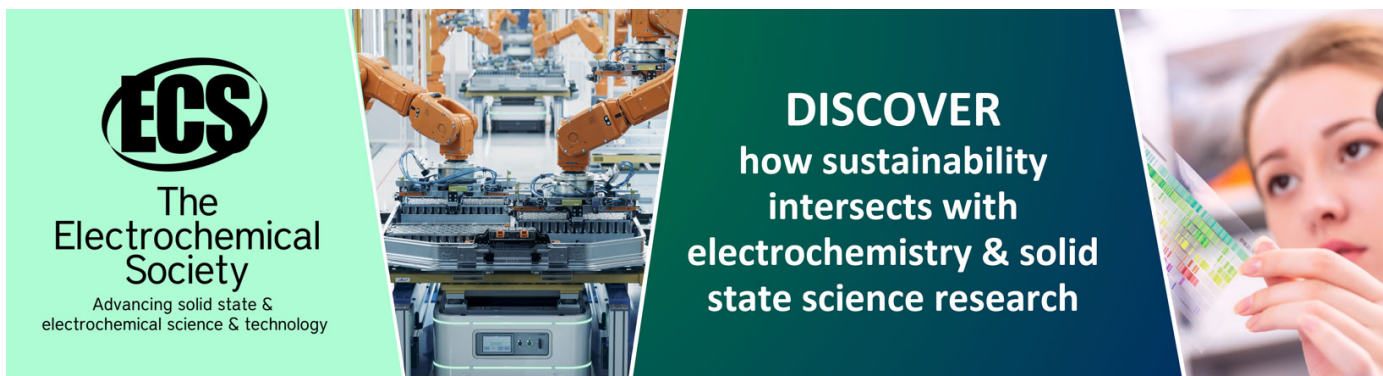
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The Research about Preparation of High Purity Hexachlorodisilane

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Abstract. This article demonstrated a technology for producing high purity hexachlorodisilane what is one raw material of Semiconductor industry, which using the method of combination adsorption with rectification, whose material was from polysilicon residues of polysilicon company. This technology could remove most high boiling points chloro-silane impurities and metal impurities effectively. The purity of Si_2Cl_6 produced by this technology can be up to 99.9%, the content of metal impurities can be low at 4ppb, which can meet the requirement of industry using completely. The technology extends the routes of Si_2Cl_6 in localization, having the advantages of simple process, continuous operation, and large capacity and so on.

Keyword: Hexachlorodisilane; Purification; Adsorption

1. Introduction

The Improved Siemens method is the mainstream process of polysilicon production, because of its advantages such as stable performance, closed circuit, and low dangers. However, it also can form much polysilicon residue, during the production process. If those residue is dealt with the methods of hydrolysis or leaching, it not only can cause a serious waste of resources but also cause different degrees of environmental pollution^[1,2,3]. Studies have showed that there is a large amounts of high boiling chlorosilane components in polysilicon residue, such as hexachlorodisilane (Si_2Cl_6), high boiling silicone oil and metal chloride impurities introduced from crude silica fume and catalyst, and Si_2Cl_6 is the most high value-added ingredients in there [3,4].

Si_2Cl_6 is an efficient deoxidizer and a raw material for producing disilane. It can be used to produce amorphous silicon film, optical fiber raw materials, glass, and mosi2 and so on. For Si_2Cl_6 , the silicon nitride film is the most important application. Compared with the traditional dichlorosilane which is used to produce nitrogen by silane vapor deposition. The temperature and deposition pressure of Si_2Cl_6 vapor deposition method is much lower, the efficiency is much higher and the density, Insulation, corrosion resistance and compatibility of the film obtained are more better^[5,6,7]. Therefore, how to



recycle the Si_2Cl_6 in chlorosilane residues economically and environmentally will become a new growth point of polysilicon enterprises.

In foreign, there are many studies for the recycling of Si_2Cl_6 from polysilicon residue. Ishikawa K^[8] proposed a way to prepare high purity Si_2Cl_6 which used the method of distillation to enhance the purity of Si_2Cl_6 , after one adsorption(activated carbon) technology was employed. S Kirii^[9] also proposed a method for the preparation of high purity Si_2Cl_6 by a distillation purification process containing a different cascade of purification towers. Knies^[10] of WACKER studied an adsorption united with distillation process to separate the polysilicon residue. WACKER also discloses a method for preparing high purity Si_2Cl_6 by making SiHCl_3 synthesis and be heated in a fixed apparatus. But so far, there is no mature and stable production process in the domestic, and the Si_2Cl_6 used in the domestic also depend on foreign importing totally.

In this paper, it demonstrated one technology for preparing high purity Si_2Cl_6 using the process of purification combined with adsorption to polysilicon residue, taking some one polysilicon enterprises in Luoyang as an example. This technology successfully achieved industrial production, extended the production line and competitiveness, and enriched the localized process routes of Si_2Cl_6 .

2. Experiment

2.1. Preparing high purity Si_2Cl_6

The process first makes polysilicon residue containing Si_2Cl_6 (40wt%) into the 1# purification column (D1) to remove the heavy components (mainly some higher boiling points metal impurities and high boiling point components), and then takes product from tower top containing a large amount of SiCl_4 to enter the 2# purification column (D2) for further separation. In this way, the low boiling point SiCl_4 will be withdrawn from the top of the column, the Si_2Cl_6 crude product will be produced in the tower kettle, and the purity of the Si_2Cl_6 crude product through once purification can be achieved above 95%.

After first purification, the purity of Crude distillation product has been greatly improved. Crude distillation products will be introduced into the 3# tower (D3) to remove heavy components again in the tower kettle, and the tower top product will go into the 4# tower (D4) for further purification and separation. In the 4# tower, low boiling points materies can be obtained from the tower top, and the Si_2Cl_6 distillation products can be got from the tower kettle. The purity of distillation product can be stabilized at up to 99.9%.

To be sure, the 1, 2 # tower is the plate tower, and 3, 4 # tower is the efficient packing tower. And system should be operated in the protected of inert gas such as high purity nitrogen, the kettle temperature should be controlled at 155 -180 °C, and the reflux ratio should be controlled at 2-10.

Subsequently, the rectification product is adsorbed in the stainless steel adsorption column (S1) filled with molecular sieves to reduce the content of metal impurities for obtaining an impurity content (<4 ppb) Si_2Cl_6 products at the protected of inert gas, the process showed in Figure 1.

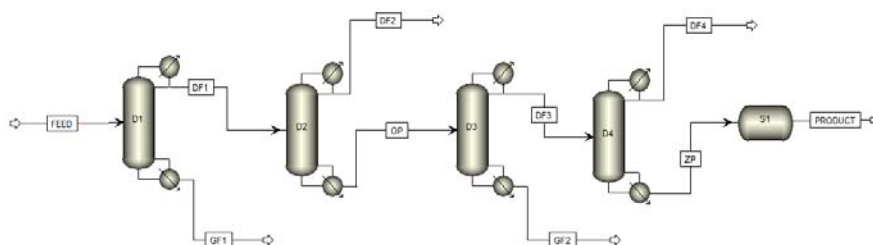


Figure 1. The process flow diagram of Si_2Cl_6

2.2. Analysis and Determination

Based on the technology, it designed an on-line and closed sampling device, which guarantees the isolation of the external environment during the sampling inspection, and reduces the risk of pollution from the outside environment. The content of the constituents in the Si_2Cl_6 sample prepared by this process was tested using GC (7890A, Agilent) and the metal impurity content in the Si_2Cl_6 sample was measured using ICP-MS (7700, Agilent). And the process was analyzed by the above testing equipment.

3. Results and discussion

3.1. Rectification

Distillation is a technology of using the different bubble points and dew point of different components of the mixtures and of going through continuous gasification and condensation to achieve the effect of gas-liquid separation. Developing so far, distillation operation process has been widely used in various fields of chemical production, becoming the basic solution of chemical separation operation. Distillation technology has simple operation, mature technology, high self-control, strong production capacity and other characteristics. For the polysilicon production, the distillation process is widely used in the chlorosilane separation and purification process. The effect of distillation purification depends on the number of cascades, the number of plates and the reflux ratio of the purification column [13,14].

Using the process, we distilled Si_2Cl_6 raw materials many times by four cascade purification towers. The GC spectrum of components in the purified product after purification was showed in Fig.2, The results of the content of the components are showed in Table 1.

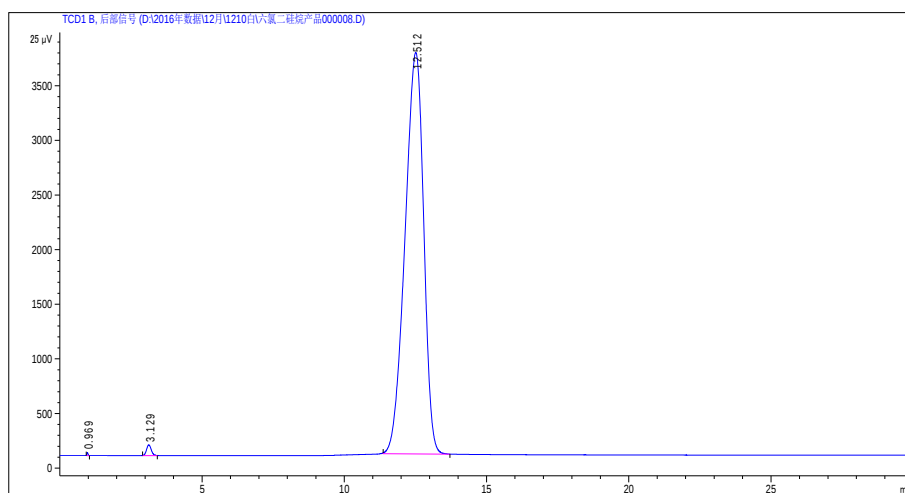


Figure 2. The GC picture of product after purification

Table 1. The content of Si_2Cl_6 after purification

Sample	SiHCl_3 (wt%)	SiCl_4 (wt%)	Unknown high Boiling point impurities (wt %)	Si_2Cl_6 (wt%)
Raw material	0.35	49.75	9.7	40.2
Crude Distillation Product	0.10	3.41	0.99	95.5
Distillation Product	0.02	0.04	0.04	99.9

It can be seen that the purity of the crude product Si_2Cl_6 through once purification is 95.5wt% and the content of unknown high boiling point impurities can be reduced to 0.99wt%, which can meet the using requirement of Si_2Cl_6 . After the second purification, the content of the distillation product has been 99.9wt%, the content of unknown high boiling point impurities can be reduced to 0.04wt%, the content of SiHCl_3 and SiCl_4 can be reduced to 0.02wt% and 0.04wt%, fully meeting the requirements of the use of Si_2Cl_6 .

This result indicates that if using some required four cascade purification towers to distill the polysilicon system residues with 40.2wt% Si_2Cl_6 , the product obtained can satisfy the requirements of industrial use of Si_2Cl_6 and the purification effect is better than that of two cascade purification towers.

The results of the metal impurities in the purified product and the raw material are showed in Table 2. It can be seen that content of impurities in the crude product is much lower than that of the polysilicon residue containing 40.2wt% Si_2Cl_6 , and the metal impurity content of the rectified product after re-purification is substantially reduced again with respect to the content of primary purified product. The results showed that most of the metal impurities were effectively removed after the purification of the polysilicon residue through the four cascade purification towers, and the purification effect of four cascade purification tower was better than that of the two cascade purification towers.

Table 2. Content of metal impurities in raw material and product (ng/g)

Sample	B	P	Al	Fe	Mg	Cr	Ni	Cu	Zn	Ti
Raw material	23.82	23.51	292	158.7	4.47	43.38	20.97	18.38	9.08	31.30
Crude Distillation Product	1.15	8.63	19.92	31.46	0.65	4.86	1.97	0.58	0.54	1.92
Distillation Product	0.60	2.22	2.67	6.66	0.54	0.86	0.40	0.16	0.17	1.60

The contents of Al, Fe, P are higher or even beyond the standard, which may because that some gaseous impurities can stay at surface of material because of their intermolecular force with pipeline. When the system is running, these impurities components will escape and pollute the process. The content of pollutants will be different with the difference of chemical composition and surface roughness in the material surface. In particular, the degree of pollution is increased due to the increase of the roughness, and the diffusion of the pollutant is mainly caused by welded defects and the pipe joint and other parts. In addition, dead zones caused by unreasonable design and component selection can pose a serious threat to the cleanliness of the system, which may because the dead zone is filth and it cannot be cleaned cleanly when the system is scavenged, usually cannot result in meeting the required after a long time scavenging and discharge^[14,15]. Therefore, when installing system, it must ensure a reasonable design firstly; before operating, the system have to replace the purge thoroughly to ensure that the system has the required cleanliness level.

3.2. Adsorption

The adsorption operation is a separation process in which metal impurities are removed with the difference in affinity of impurities in the adsorbent and raw material. Developing so far, adsorption has been widely used in chemical industry, metallurgy, pharmaceutical and other fields, becoming one basic solution of separation unit operation^[16]. In the polysilicon production system, the adsorption operation has been widely and effectively applied to removing B, P and other metal impurities. In the Si_2Cl_6 production process, the adsorption operation can also be used to reduce the metal impurity content.

The rectification product was subjected to adsorption treatment for 30 min to further reduce the content of metal impurities by using a two-stage stainless steel material filled with molecular sieves adsorbent. The results of the adsorption test are showed in the Figure 3.

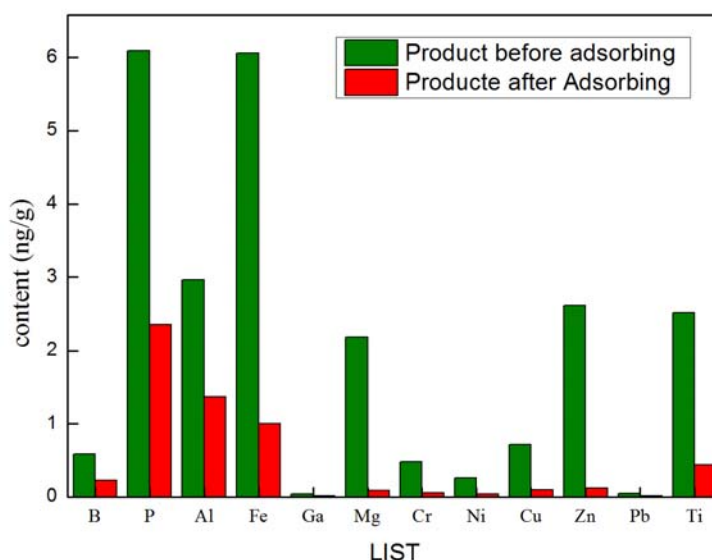


Figure 3. Content of metal impurities before and after adsorption

It can be seen that the content of metal impurities after ultrasonic adsorption treatment is lower than 4ppb, most indexes even lower than the detection limit. The results show that molecular sieves adsorbent can reduce the content of metal impurities obviously, and content of metal impurity in the product after adsorption can meet the requirement of industrial application.

4. Conclusion

In this paper, a process was proposed to prepare Si_2Cl_6 using polysilicon system residue, which promoted the efficient use of polysilicon system residue and enriched the localized process route. The process consisted of four cascade purification towers and adsorption units. The raw material was purified by fractional distillation through a four-stage purification columns. The purity of the rectified product can be up to 99.9%. The metal impurities of the rectified product was separated and adsorbed through adsorption column, and the content of metal impurities were completely reduced to within 4ppb to meet the requirements of industrial applications.

At the same time, this article also pointed out that when installing equipment, it needs to control the equipment of pipe's selection and design. Before running, it needs to scavenge and replace system completely to ensure that system has high level cleanliness. At the same time, it can choose adsorbent (activated carbon) with better adsorption performance to reduce the content of metal impurity further.

Acknowledgments

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