Thermodynamic Fundamental of Purification of Silicon

XU Wen-ting, MA Wen-hui, YANG Bin, DAI Yong-nian
(Faculty of Materials and Metallurgical Engineering, Kunming University of Science and Technology// National Engineering Laboratory of Vacuum Metallurgy, Kunming 650093, China)

Abstract: Along with the rapid development in photovoltaic market, silicon is used to produce solar cell more than 90% as the starting material for crystalline silicon wafers. This article is to discuss the academic thermodynamics in the process of silicon purification, which contains acid leaching, vacuum refining, directional solidification. The feasibility in this process was discussed based on thermodynamics and phase diagrams. Besides, authors have done some experiments on metallography to prove the process. The purpose is in order to do some favor for update existing silicon refining technology, and seek a low-cost process to produce solar grade silicon (SOG-Si) which is different with SIEMENS technique.

Key words: silicon purification; solar grade silicon; thermodynamic
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As materials for solar cells, multicrystalline silicon always holds a dominate station, and this status will stand for a long time, at least for twenty years. In present, the most production of solar-grade silicon in the world is modified SIEMENS. But this process is limited to current production by its raw and processed materials and its costs. So, this article is to discuss another possible metallurgical method exploited by authors[1], which is based on theoretical analysis.

1 Raw and processed materials

Silicon for producing solar cells requires that the content of impurities must be lower than 1. Otherwise, the conversion efficient of multicrystalline silicon solar cells will be effected deeply. To obtain SOG-Si is refining metallurgical silicon (MG-Si). And there are 99.8% silicon in MG-Si, besides some impurities: B or P (20 ~60), Fe (1600 ~3000), Ca (400 ~900), Ti (150 ~ 200), Al (1200 ~ 4000), C and Na, etc[1].

2 Thermodynamic analysis

2.1 Hydrometallurgical process

The purity of silicon could be higher than 99.9% after hydrometallurgical process. So it is very suitable for preliminary purification, which is shown in Fig.1.

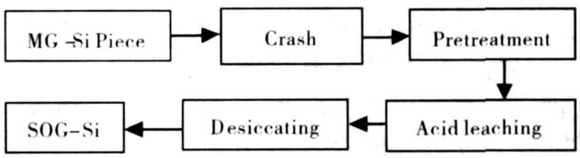

Fig.1 Schematic diagram of hydrometallurgical pretreatment to produce upgrade metallurgical grade powder

The appropriate granularity is 50 ~ 70 μm. In preliminary, impurity iron will be eliminated by a special method.

2.2 Vacuum distillation

Vacuum distillation is an efficient way to eliminate impurities in silicon, such as calcium, magnesium, phosphorous, which is based on the saturation stream pressure of pure substance[2].

$$\lg P^{*} = AT^{-1} + B\lg T + CT + D \quad (1)$$

Where, P^{*} is saturation stream pressure of pure substance, A, B, C, D is constant, respectively, all these data can be found in related handbooks[3].

2.3 Directional solidification

Most of impurities will be removed by this way, which determined by the coefficient k_0. And if we repeat this process running for five times, the impurities in silicon will be down to 1×10^{-9}[3]. However, the

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作者简介：徐文婷（1983年生），女，研究生；通讯联系人：马文会；E-mail: mwhui@kmust.edu.cn

increased times means the increased cost, which must be considered. The expression of equilibrium separation coefficient k_0 is:

$$k_0 = \frac{C_s}{C_l} \qquad (2)$$

Where, C_s and C_l are the impurity concentrations in solid phase and liquid phase respectively. As shown in Fig.2.

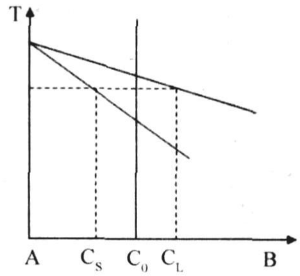

Fig.2 Partial of binary phase diagram

But in actual process of directional solidification, the real equilibrium is different, so we give the distributing of impurity along with the silicon ingot as following[4]:

$$C_a = k_0 C_l (1 - x)^{-(1-k_0)} \qquad (3)$$

Where, C_a is the concentration of impurity along with the solidification direction, x is the length of solid silicon ingot. And mostly k_0 of impurities are given in following table 1[4-5].

Tab.1 Segregation coefficients k_0 of impurity in silicon at thermodynamics equilibrium

Impurity	k_0	Impuriy	k_0
B	0.8~0.9	Li	1×10^{-3}
Al	2×10^{-3}	Zn	1×10^{-5}
Ca	8×10^{-3}	Cu	4×10^{-4}
In	4×10^{-4}	Au	2.5×10^{-6}
P	0.35	Ni	2.5×10^{-5}
As	0.30	Co	8×10^{-5}
Sb	2.3×10^{-2}	Ta	1×10^{-7}
Bi	7×10^{-4}	Fe	8×10^{-6}
Sn	2×10^{-2}	O	0.5

According to the data given by table 1, removable impurities are confirmed. In practical operation, the result will be effecting by temperature control and the velocity control.

3 Experimental results

Prepare silicon ingot by the method above mentioned. Then do a metallographic analysis. The steps are polishing the specimen of silicon and corrupting the specimen with CP4 solution for ten seconds in room temperature. After washing and drying, observe the specimen with optical microscope, as shown in Fig.3.

From Fig.3, silicon grain boundary can be seen clearly, and lots of etch pits. Cause the CP4 solution is a preferential one, which lead to erosive phasic difference.

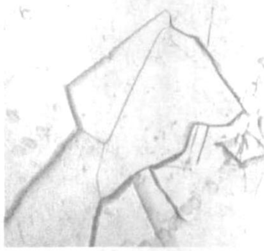

Fig.3 Image of micro after leaching 200×

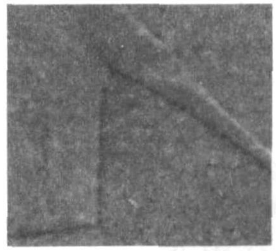

Fig.4 Image of SEM after leaching 2000×

From Fig.4, there is all silicon in the surface confirmed by energy spectrum analysis. The grain boundary can be seen clearly. And many outcrops of dislocation also can be seen in this figure. To explain why there are too many dislocations, It cause the control precision isn't on a better condition. And the lifetime of minority carriers will decrease. Based on some researches[6], the size of cross-section of grain boundary about 2 mm will not effect the efficiency of solar cells. Therefore, we need to control the process and get suitable size of the columnar grain, but its need to avoid the appearance of close grain.

4 Conclusion

We give some thermodynamics foundation to produce multicrystalline silicon by metallurgic technology. And based on the analysis, an effective process to produce SOG-Si from MG-Si has been proposed.

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硅提纯的热力学基础

徐文婷，马文会，杨 斌，戴永年
(昆明理工大学 材料与冶金工程学院 //真空冶金研究所，云南 昆明 650093)

摘 要：随着光伏产业的发展，硅作为生产晶体硅片太阳电池的基础材料，其应用已经超过了 90%。从热力学基础对提纯硅的冶金过程进行讨论，其中包括酸浸、真空精炼和定向凝固，并基于热力学相图对这一过程的可行性进行了讨论。除此之外，通过金相分析对过程可行性进行证明。目的在于寻找一种区别于西门子法的低成本的生产太阳能级硅的工艺过程。

关键词：硅提纯；太阳能级硅；热力学
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添加镍粉球磨对 $Mg_{17}Al_{12}$ 合金相结构及电化学储氢性能的影响

肖学章，葛红卫，陈立新，王新华，李寿权，王 丽，陈长聘
(浙江大学 材料与化工学院材料系，浙江 杭州 310027)

摘 要：研究了 $Mg_{17}Al_{12}$铸态合金和 $Mg_{17}Al_{12}$ + x% Ni (x = 50 ~ 200) 球磨复合物的相结构和电化学性能。结果表明，$Mg_{17}Al_{12}$-Ni复合物的相结构和放电容量主要取决于复合物中镍粉的加入量。加入的镍粉越多，越利于非晶结构的形成，其放电容量就越大。球磨 120 h的 $Mg_{17}Al_{12}$ + 200% Ni复合物在 303K的放电容量高达 658.2 mAh·g^{-1}（除去镍粉的质量）。

关键词：储氢合金；$Mg_{17}Al_{12}$；球磨；电化学性能；相结构
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