Study on the surface cleaning process of polysilicon fleece after diamond wire cutting

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Abstract. In the texturing process of diamond wire polycrystalline silicon solar cells optimizing the preparation of the light-trapping texture structure needs to add texturing additives. In this thesis, the phenomenon which additives remain on the surface of the silicon wafer was found through the contact angle test. The texturing silicon wafer are cleared by ultrasound with water and absolute ethanol respectively, and the change of contact angle was used to verify the cleaning effect of the two cleaning processes. The research results show that additives remain on the surface of the texturing silicon wafer, and ultrasonic cleaning with absolute ethanol can significantly improve the cleanliness of the flock sheet.

1. Introduction

Diamond wire silicon wafer cutting technology can reduce the cost of silicon wafers by 0.4-0.6 yuan compared with mortar wafers, and has many advantages such as environmental friendliness, less loss, and high slicing efficiency. It is now recognized as an advanced slicing technology. Diamond wire silicon wafers have been fully promoted through anisotropic alkali etching in the cutting of monocrystalline silicon wafers. However, due to the presence of an amorphous silicon layer on the surface of the diamond wire cut polysilicon wafer [1, 2], it is difficult to prepare a light trapping texture on the surface of the silicon wafer when the traditional polycrystalline silicic acid texturing process is used for isotropic corrosion [3, 4], resulting in the problem of high reflectivity on the surface of the silicon wafer and low photoelectric conversion efficiency of the solar cell. At present, by adding diamond wire polysilicon texturing additives to change the interfacial tension and wetting effect between the etching solution and the silicon wafer, in the industry a special surface structure with excellent light trapping performance has been realized, and the photoelectric conversion efficiency of the solar cell has been improved.

In addition to constant temperature and humidity, the production process of crystalline silicon solar cells has stricter requirements on the cleanliness of the production environment. Potential pollution in each process of battery production, such as impurity particles, metal ions, organic residues, dust, etc., will reduce cell performance. To obtain high-quality polycrystalline silicon solar cells, the cleanliness of the entire production process of silicon wafers must be ensured. At present, the additive components on the market are mainly organic substances such as surfactants, polymer diffusing agents, and corrosion inhibitors. These components may remain on the surface of the silicon wafer, making it difficult to
remove the oxide layer and related dirt. Therefore, the cleaning process of residual additives on the surface of the polysilicon fleece after diamond wire cutting has become an important research direction.

Surface wettability is one of the important characteristics of a solid surface, which is mainly determined by the chemical composition of the solid surface and the surface microstructure [5,6]. Since the texturing additives are hydrophilic materials, any residues will affect the surface wettability of the texturing silicon wafer. The wettability of the solid surface is usually measured by the contact angle of the liquid on the solid surface. The contact angle is generally defined as the angle between the tangent of the droplet surface at the solid-liquid-gas three-phase junction and the solid surface, as shown in Figure 1.

\[ \theta = \gamma_{lv} - \gamma_{sv} \]

\[ \gamma_{lv} \]

\[ \gamma_{sv} \]

\[ \gamma_{st} \]

\[ \text{gas} \]

\[ \text{liquid} \]

\[ \text{solid} \]

This thesis characterizes the additive residue on the surface of the diamond wire additive texturing silicon wafer (silicon wafer after texturing process) through the contact angle test. The experiment verified the cleaning effect of different cleaning processes on the additive residual components, and obtained a kind of silicon cleaning method of the additive residue on the surface of the silicon wafer, thereby improving the cleanliness of the surface of the solar cell.

2. Experiment

2.1. Experimental equipment and reagents

The main experimental materials and equipment used are shown in Table 1 and Table 2 respectively.

| Name               | Molecular formula/model | Content W/% | Origin                                      |
|--------------------|-------------------------|-------------|---------------------------------------------|
| P-type silicon wafer | Si                      | >99.999     | GCL-Poly Energy Holdings Limited            |
| Hydrofluoric acid   | HF                      | 49          | Wuxi Dongfeng New Energy Technology Co., Ltd.|
| Nitric acid         | HNO3                    | 68          | Wuxi Dongfeng New Energy Technology Co., Ltd.|
| Absolute ethanol    | CH3CH2OH                | >99.5       | Wuxi Dongfeng New Energy Technology Co., Ltd.|
| Additive            | PT-013-D                |             | Hangzhou Flying Deer New Energy Technology Co., Ltd.|
| Deionized water     |                         |             | Self-made                                   |
Table 2. Main experimental equipment.

| Name                        | Model | Origin                     | Application                                  |
|-----------------------------|-------|----------------------------|----------------------------------------------|
| Texturing equipment         | SCHMID| The SCHMID Group           | Preparation of texturing silicon wafer       |
| Laser scanning              | LEXT 4000 | Olympus Corporation       | Morphological characterization              |
| confocal microscope         |       | Shanghai Suolun Information Technology Co., Ltd. |                                  |
| Contact angle meter         | SL1000| Contact angle test         |                                              |
| Ultrasonic cleaning machine | SK1200H| Shanghai Kudos Ultrasonic Instrument Co., Ltd. | Wafer surface cleaning                    |

2.2. Experimental method

2.2.1. Preparation of texturing silicon wafer. Place the original silicon wafer in a certain ratio of HF:HNO3: H2O mixture, and remove the damage layer produced by the cutting of the silicon wafer surface at a certain temperature to prepare a light-trapping suede structure. The texturing process of the comparison group and the experimental group is shown in Table 3.

Table 3. Texturing process with different additives.

| ITEM          | Solution ratio | Process conditions |
|---------------|----------------|--------------------|
|               | HF (L) | HNO3 (L) | DI (L) | additive (L) | temperature (°C) | react time (s) |
| control group |        | 55       | 220    | 110         | 0                | 7               | 65            |
| experimental  |        | 70       | 200    | 110         | 2.8              | 7               | 65            |

2.2.2. Cleaning process. The experimental groups were divided into three groups, namely experimental group 1, experimental group 2 and experimental group 3. The silicon wafers in experimental group 2 and experimental group 3 were ultrasonically cleaned with water and absolute ethanol for 3 minutes, respectively. After that, the two groups of silicon wafers were washed with water for 2 minutes and dried.

2.2.3. Contact angle test. Use a contact angle meter to measure the contact angle of texturing additives on the comparison group. At the same time, a contact angle meter was used to measure the contact angle of water on the texturing silicon wafer of the control group, the experimental group 1, the experimental group 2, the experimental group 3, etc. respectively.

3. Experimental results and discussion

3.1. Deionized water, texturing additives and silicon wafer wettability

Using a contact angle meter, deionized water and texturing additives were dropped on the texturing silicon wafer of the contrast group without texturing additives, and the average water contact angles of the two groups of samples were 102° and 68°, respectively. The results show that the contact angle of deionized water on the surface of the silicon wafer is large, and the wettability is low; the contact angle of the texturing additive on the surface of the silicon wafer is small, and the wettability is high. Since the main components of texturing additives are surfactants and water, surfactants contain hydrophobic groups (hydrophobic alkyl groups) and hydrophilic groups (polyoxyethylene chains) [7]. That is to say,
the texturing additives used in the experiment contain hydrophilic groups to increase the wettability of water and the surface of the silicon wafer. Figure 2 shows the contact angle test chart of water and texturing additives on the texturing silicon wafer of the contrast group.

![Contact Angle Test Chart](image1)

(a) deionized water  (b) texturing additives

**Figure 2.** Test chart of average surface contact angle between different solvents and silicon wafer.

3.2. **The effect of texturing additives on the textured surface structure of silicon wafers**

Figure 3 shows the test chart of the textured surface structure of the texturing silicon wafer with and without texturing additives. It can be seen from the figure that the width of the textured surface of the two sets of samples is 2000-3000nm. By comparing the densities of "worm-holes" on the texturing silicon wafer with and without texturing additives, it can be seen that compared with the control group, the density of the "worm-holes" in the experimental group after the addition of texturing additives has increased significantly, the surface area has also been greatly increased.

![Textured Surface Structure Diagram](image2)

(a) control group  (b) experimental group

**Figure 3.** The textured surface structure diagram of the texturing silicon wafer of different texturing processes.

3.3. **Verification of additive residues on the surface of the texturing silicon wafer**

According to the model analysis of Wenzel [8], the surface area of the textured surface of the texturing silicon wafer with texturing additives is larger than that of the texturing silicon wafer without texturing additives. In this case, the water contact angle of the silicon wafer surface with texturing additives should be greater than that of no texturing additives. According to this theory, the water contact angle of the silicon wafer surface was tested for the two kinds of velvet back wafers, and the test results are shown in Figure 4. Through the test, the average water contact angles of the two groups of samples are 102° and 75° respectively; the test results are exactly the opposite of the theory. Through the experiment
and the analysis of 3.1, it can be seen that the hydrophilic group in the texturing additive is not completely cleaned after texturing, and part of it remains on the surface of the silicon wafer. Due to the effect of the hydrophilic group of the texturing additive, the hydrophilic properties of the surface of the silicon wafer were improved.

![Figure 4](image)

Figure 4. The textured surface structure diagram of the texturing silicon wafer of different texturing processes.

3.4. Verification of different cleaning schemes for texturing silicon wafer

Figure 5 shows the test diagrams of the contact angle of the silicon surface of the experimental group 2 and the experimental group 3 after the textured surface was cleaned with different cleaning schemes. Through the test, the average water contact angles of the two groups of samples were 94° and 110°, respectively. Compared with experimental group 1, it was found that after washing with water and absolute ethanol the contact angle of the textured surface of the texturing silicon wafer increased significantly and the wettability is reduced. The results show that the residual amount of additives on the surface of the silicon wafer is reduced after the above two methods are used for cleaning.

By comparing with the silicon surface contact angle of the control group, it is found that the cleaning effect of using absolute ethanol is better than that of deionized water cleaning. This is because the main components of the additives are organic substances such as surfactants, polymer diffusing agents, and corrosion inhibitors. Using the rule of the likes dissolve each other, adding organic solvents such as ethanol during the cleaning process can remove organic impurities on the surface of the silicon wafer, and the residual additives on the surface of the texturing silicon wafer after cleaning are reduced. At the same time, in the ultrasonic cleaning process, cavitation occurs due to tiny bubbles, which continuously generates instantaneous high pressure, like a series of small explosions that constantly bombard the surface of the object, causing the dirt in the object and the gap to quickly peel off [1]. The van der Waals force between the surfactant of the additive and the silicon wafer is also breaked, and the additive residue on the surface of the flocking wafer is cleaned thoroughly.
Figure 5. The contact angle of water on the surface of silicon wafers with different cleaning methods

4. Conclusion
By measuring the surface contact angle of the texturing silicon wafer with and without texturing additives, We have found that the hydrophilic group remains on the back of the additive texturing silicon wafer. After ultrasonic cleaning with water and absolute ethanol, the residual amount of additives on the surface of the silicon wafer can be effectively reduced.

At present, major cell manufacturers have not simple and effective judgments on additive residues. The contact angle method proposed in this article is simple, non-destructive, fast, and inexpensive. It is a test that is worthy of promotion. the way.

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