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Mini Review

Polymer Additives Promoted Texturization on Monocrystalline Silicon for Solar Cell

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Abstract

The solar photovoltaic was well recognized as one of the major constituent parts in future green energy system to achieving carbon neutrality. Among various technological routes to improve photoelectric conversion efficiency, rational surface texturization on monocrystalline silicon is one of the most crucial and fundamental processing steps, so as to well control the micro/nano surface structure and obtain lower light reflectivity. Chemical wet etching was the current mainstream technology in photovoltaic industry, yet there is an urgent need to update green, efficient, customized texturization additives to meet the industrial demand. This minireview summarizes the history, key breakthrough and recent advance in texturization additives based on organic and polymer molecules as crucial chemicals, and provides perspective to development directions of future texturization additives.

Introduction

To achieve the ambitious goal of "peaking carbon emissions and achieving carbon neutrality", solar photovoltaic has become one of the fastest developing renewable energy sources in recent years due to its significant advantages such as zero carbon emissions, economic feasibility, and sustainability [1]. It was widely regarded as the most promising permanent energy source for humanity in the future [2]. In the next three decades, with technical progress and more and more solar farms, approximately 25% of the world's total electricity needs will be provided by solar photovoltaic by 2050 [3]. The continuous improvement on energy conversion efficiency of photovoltaic cell and then steadily reduce on electricity prices have become a major issue related to green and sustainable development of energy, environment and economy. Among various technological routes including PERC, TOPCon, HJT, IBC, as well as new perovskite stacked photovoltaic cells, rational surface texturization on monocrystalline silicon is one of the most crucial and fundamental processing steps, so as to well control the micro/nano surface structure and obtain lower light reflectivity [4].

Academic and industrial circles have widely explored a variety of methods for texturization on monocrystalline silicon, such as chemical wet corrosion, reactive ion etching, mechanical grooving, electrochemical corrosion, laser etching and so on. The chemical wet etching that uses strong alkali to react with silicon, processes combined advantages covering simple equipment, low cost, easy control on the reaction, and great suitable for industrial scale production, and was adopted as the mainstream technology in photovoltaic industry at present. Due to the differences in the structure of the hanging bonds at different crystal faces, the alkali corrosion rate of (100) crystal face is faster than that of (111) crystal face. Such anisotropic alkali corrosion forms positive random "pyramid" structures composed of four (111) faces [5]. From the analysis of the actual working conditions of existed production line, in order to speed up the reaction process and improve the production efficiency and save the cost, the NaOH or KOH solution with a concentration of 1~2 wt% was used as the etchant, coupled with a high reaction temperature of 80~90°C. Under such violent reaction conditions, the OH⁻ is continuously consumed and results in concentration difference at the surface interface of silicon wafer. In addition, a large number of bubbles and silicates were continuously generated, leading to irregular pyramid structure and size on the monocrystalline silicon surface, which seriously affects the light absorption efficiency. Subsequently, various types of additives have been introduced to regulate and optimise the core texturization process of silicon wafers.

Discussion

In the initial stage, organic small molecule of alcohol derivants, organic bases, and inorganic salts have been explored as different additives for the NaOH or KOH etching solution to obtain improved texturization effect. Among them, isopropyl alcohol was the first that has been put into industrial application, yet there are several inherent drawbacks including large size of pyramid, limited uniformity, low boiling point caused easy volatility, as well as toxicity leading to high cost of post-treatment. In a paralleled way, organic and polymer molecules were also been screened to develop effective texturization additives. As early as 2011, sodium dodecyl sulfonate (CH₃(CH₂)₁₀CH₂SO₃Na) solution was first proved to be a useful additive, uniform pyramids with average size of 2 μm were formed on the single crystal silicon wafer [6]. Subsequently, a very small amount of modified starch with concentration of 0.02% was introduced as functional additive by Ding et al to remove white spots on the surface of silicon wafers [7]. Zubeľ and coworkers proposed a co-solubilization mechanism of surfactant molecules in alcohols. The surface of silicon wafer was etched by TMAH solution using mixed additives of Triton and 2-butanol. The results showed that the TMAH solution containing butanol seemed to be superior than that of isopropyl alcohol, in reducing the roughness of the etched surface. While the additional Triton facilitate the best surface roughness (Ra = 0.0322 μm for Si(110)) [8]. Gong et al. developed a new type of small tower on the surface of monocrystalline silicon



by texturing it with an alkaline solution containing special additives. The surface wettability and morphology were modified by 5.0%wt $C_{12}H_{25}NHCH_2CH_2COO-Na$ and 5.0%wt $C_{32}H_{35}O_{10}$ to obtain new surface microstructure. The reflectivity was just 10.12% in the range of 400-1000 nm [9]. Wang et al. added additives such as acids (tartaric acid, boric acid) and surfactants (methyl cellulose, sodium dodecyl sulfonate, polyethylene glycol PEG 400) to the traditional alkali-alcohol texture system and study the effect of additive content on the morphology and reflectivity of the texture surface [10].

The addition of sodium dodecyl sulfonate and PEG 400 can result in smaller pyramid structures. A possible explanation is that they are all linear structures with small steric hindrance and strong adsorption ability on silicon wafers. In another report, a non-ionic surfactant NC-200 (100% polyoxyethylene alkyl phenyl ether) was added to a 5% TMAH solution, and significantly improved the roughness of the (100) (110) surface, but it also reduced the etching rate which is unfavorable for process production [11]. More recently, sodium dodecyl benzene sulfonate (SDBS) [12], sodium lignosulfonate [13], cyclodextrin(CD) [14], and sodium methylene naphthalene sulfonate(NNO) [15] have been widely used as functional additives taking advantage of their sulfonic acid groups. Rui et al. used sodium lignosulfonate as an auxiliary agent for the first time to obtain uniform and dense nucleation points, while adding cyclodextrin and sodium carbonate to regulate the etching rate and pyramid size [13]. The wet etching process using this additive can produce a uniform pyramid structure on the Si surface in only 7 minutes, which is at least 3 minutes shorter than the conventional wet etching process. The battery efficiency can reach 22.81%. The outer wall of cyclodextrin contains a large number of hydroxyl groups, which are hydrophilic and have strong adsorption on the surface of silicon wafers. In 2021, cyclodextrin was used to prepare industrial large-scale monocrystalline silicon PERC solar cells, with high average efficiency of 22.61% [14].

Conclusion

Looking back on the early commercial additive containing large amounts of IPA and subsequent various attempt on inorganic salts, organic bases and their mixtures, this minireview highlighted recent development of new additives using sodium lignosulfonate, sodium dodecyl sulfonate, cyclodextrin and others as key functional chemicals. With the rapid development and demand of the photovoltaic industry chain, new classes of highly efficient, green, stable and economical texturization additives have become necessities to prepare uniform, target-sized, and low-reflectivity pyramidal structures on monocrystalline silicon. New organic and polymer molecules with large molecular size and multiple functional groups are potential and valuable directions for development.

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