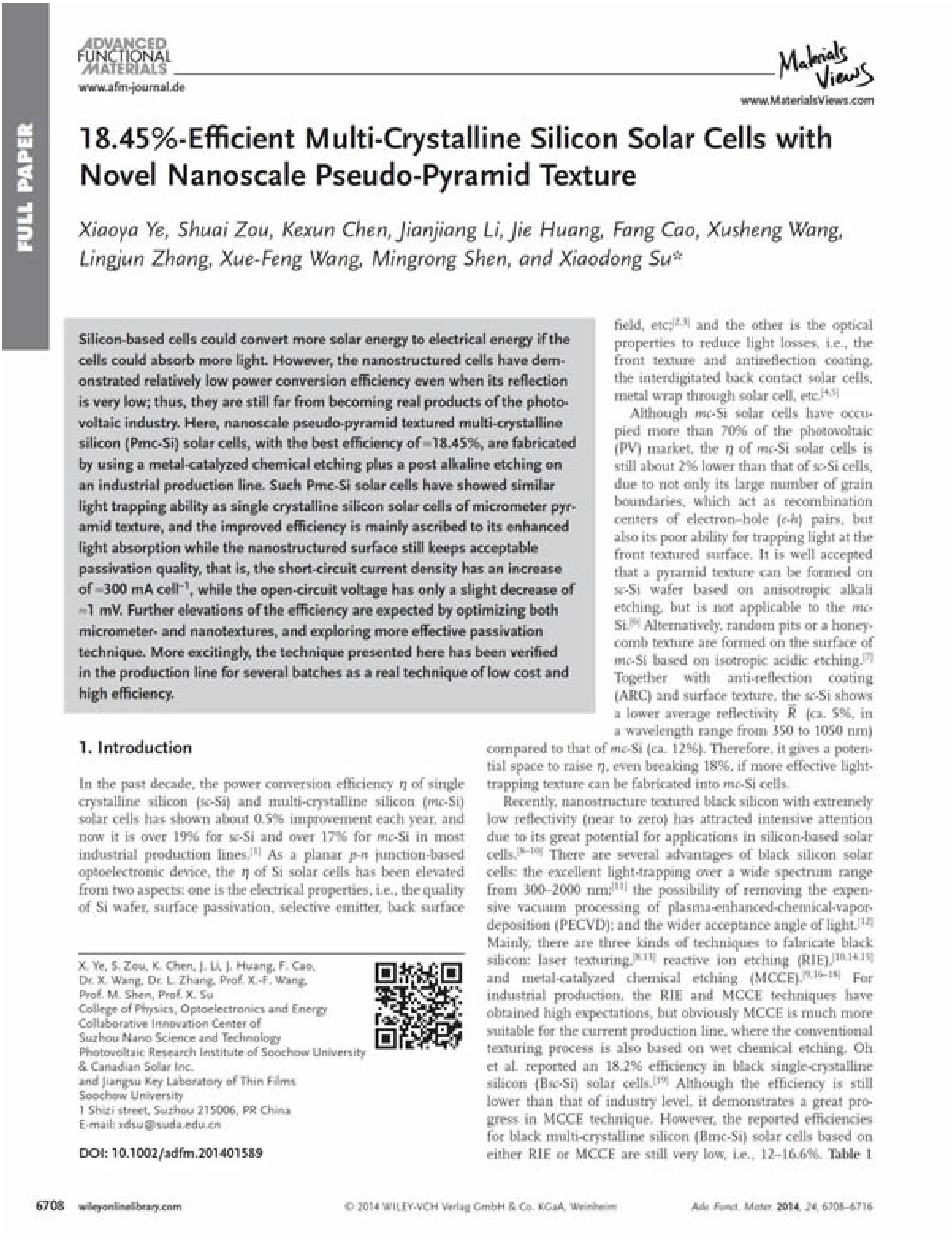
# 苏州大学苏晓东教授团队标志性系列论文 引领湿法黑硅技术产业化发展

晶硅太阳电池是当前新能源领域光伏行业的主导产品，全球年产能高达100GW。电池效率的提升有赖于电池光学和电学性能的同步提高。苏州大学苏晓东教授课题组自2012年开始研究湿法黑硅技术，通过制备独特的纳米/亚微米绒面实现了电池光学和电学性能的同步提高。湿法黑硅技术在短短几年时间里实现了大规模的产业化应用，对光伏行业的降本增效意义重大，也大大加速了我国光伏发电平价时代的早日实现。近五年团队在该领域发表论文20余篇，申请专利10余项。其中，具有里程碑意义的标志性论文如下：

2014年，在Adv. Funct. Mater.发表自主研发的湿法黑硅技术论文，首次报道湿法多晶黑硅太阳电池效率超过产线常规电池，并在合作企业阿特斯阳光电力率先实现产业化生产。



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# 18.45%-Efficient Multi-Crystalline Silicon Solar Cells with Novel Nanoscale Pseudo-Pyramid Texture

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**Silicon-based cells could convert more solar energy to electrical energy if the cells could absorb more light. However, the nanostructured cells have demonstrated relatively low power conversion efficiency even when its reflection is very low; thus, they are still far from becoming real products of the photovoltaic industry. Here, nanoscale pseudo-pyramid textured multi-crystalline silicon (Pmc-Si) solar cells, with the best efficiency of ~18.45%, are fabricated by using a metal-catalyzed chemical etching plus a post alkaline etching on an industrial production line. Such Pmc-Si solar cells have showed similar light trapping ability as single crystalline silicon solar cells of micrometer pyramid texture, and the improved efficiency is mainly ascribed to its enhanced light absorption while the nanostructured surface still keeps acceptable passivation quality, that is, the short-circuit current density has an increase of ~300 mA cell$^{-1}$, while the open-circuit voltage has only a slight decrease of ~1 mV. Further elevations of the efficiency are expected by optimizing both micrometer- and nanotextures, and exploring more effective passivation technique. More excitingly, the technique presented here has been verified in the production line for several batches as a real technique of low cost and high efficiency.**

## 1. Introduction

In the past decade, the power conversion efficiency $\eta$ of single crystalline silicon (*sc*-Si) and multi-crystalline silicon (*mc*-Si) solar cells has shown about 0.5% improvement each year, and now it is over 19% for *sc*-Si and over 17% for *mc*-Si in most industrial production lines.[1] As a planar *p*-*n* junction-based optoelectronic device, the $\eta$ of Si solar cells has been elevated from two aspects: one is the electrical properties, i.e., the quality of Si wafer, surface passivation, selective emitter, back surface field, etc;[2,3] and the other is the optical properties to reduce light losses, i.e., the front texture and antireflection coating, the interdigitated back contact solar cells, metal wrap through solar cell, etc.[4,5]

Although *mc*-Si solar cells have occupied more than 70% of the photovoltaic (PV) market, the $\eta$ of *mc*-Si solar cells is still about 2% lower than that of *sc*-Si cells, due to not only its large number of grain boundaries, which act as recombination centers of electron–hole (*e*-*h*) pairs, but also its poor ability for trapping light at the front textured surface. It is well accepted that a pyramid texture can be formed on *sc*-Si wafer based on anisotropic alkali etching, but is not applicable to the *mc*-Si.[6] Alternatively, random pits or a honeycomb texture are formed on the surface of *mc*-Si based on isotropic acidic etching.[7] Together with anti-reflection coating (ARC) and surface texture, the *sc*-Si shows a lower average reflectivity $\bar{R}$ (ca. 5%, in a wavelength range from 350 to 1050 nm) compared to that of *mc*-Si (ca. 12%). Therefore, it gives a potential space to raise $\eta$, even breaking 18%, if more effective light-trapping texture can be fabricated into *mc*-Si cells.

Recently, nanostructure textured black silicon with extremely low reflectivity (near to zero) has attracted intensive attention due to its great potential for applications in silicon-based solar cells.[8–10] There are several advantages of black silicon solar cells: the excellent light-trapping over a wide spectrum range from 300–2000 nm;[11] the possibility of removing the expensive vacuum processing of plasma-enhanced-chemical-vapor-deposition (PECVD); and the wider acceptance angle of light.[12] Mainly, there are three kinds of techniques to fabricate black silicon: laser texturing,[8,13] reactive ion etching (RIE),[10,14,15] and metal-catalyzed chemical etching (MCCE).[9,16–18] For industrial production, the RIE and MCCE techniques have obtained high expectations, but obviously MCCE is much more suitable for the current production line, where the conventional texturing process is also based on wet chemical etching. Oh et al. reported an 18.2% efficiency in black single-crystalline silicon (B*sc*-Si) solar cells.[19] Although the efficiency is still lower than that of industry level, it demonstrates a great progress in MCCE technique. However, the reported efficiencies for black multi-crystalline silicon (B*mc*-Si) solar cells based on either RIE or MCCE are still very low, i.e., 12–16.6%. **Table 1**

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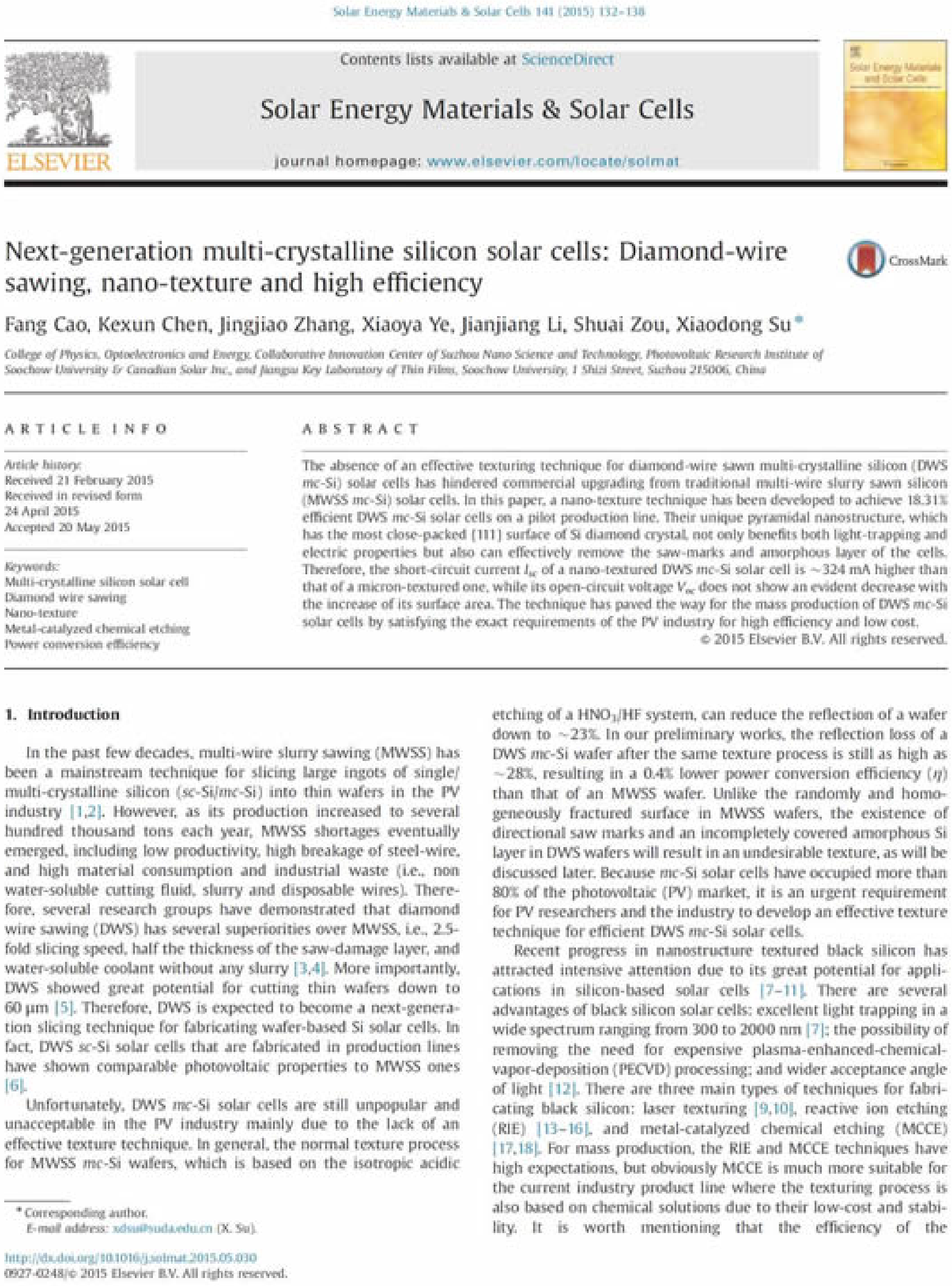
2015年，在Solar Energy Materials & Solar Cells发表论文，报道了黑硅技术能够解决下一代金刚线切多晶硅电池的制绒难题，并很快发展为金刚线切多晶硅电池的标准工艺，形成超千亿的市场。



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## Next-generation multi-crystalline silicon solar cells: Diamond-wire sawing, nano-texture and high efficiency

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ABSTRACT

The absence of an effective texturing technique for diamond-wire sawn multi-crystalline silicon (DWS *mc*-Si) solar cells has hindered commercial upgrading from traditional multi-wire slurry sawn silicon (MWSS *mc*-Si) solar cells. In this paper, a nano-texture technique has been developed to achieve 18.31% efficient DWS *mc*-Si solar cells on a pilot production line. Their unique pyramidal nanostructure, which has the most close-packed {111} surface of Si diamond crystal, not only benefits both light-trapping and electric properties but also can effectively remove the saw-marks and amorphous layer of the cells. Therefore, the short-circuit current $I_{sc}$ of a nano-textured DWS *mc*-Si solar cell is ~324 mA higher than that of a micron-textured one, while its open-circuit voltage $V_{oc}$ does not show an evident decrease with the increase of its surface area. The technique has paved the way for the mass production of DWS *mc*-Si solar cells by satisfying the exact requirements of the PV industry for high efficiency and low cost.

### 1. Introduction

In the past few decades, multi-wire slurry sawing (MWSS) has been a mainstream technique for slicing large ingots of single/multi-crystalline silicon (*sc*-Si/*mc*-Si) into thin wafers in the PV industry [1,2]. However, as its production increased to several hundred thousand tons each year, MWSS shortages eventually emerged, including low productivity, high breakage of steel-wire, and high material consumption and industrial waste (i.e., non water-soluble cutting fluid, slurry and disposable wires). Therefore, several research groups have demonstrated that diamond wire sawing (DWS) has several superiorities over MWSS, i.e., 2.5-fold slicing speed, half the thickness of the saw-damage layer, and water-soluble coolant without any slurry [3,4]. More importantly, DWS showed great potential for cutting thin wafers down to 60 μm [5]. Therefore, DWS is expected to become a next-generation slicing technique for fabricating wafer-based Si solar cells. In fact, DWS *sc*-Si solar cells that are fabricated in production lines have shown comparable photovoltaic properties to MWSS ones [6].

Unfortunately, DWS *mc*-Si solar cells are still unpopular and unacceptable in the PV industry mainly due to the lack of an effective texture technique. In general, the normal texture process for MWSS *mc*-Si wafers, which is based on the isotropic acidic etching of a $HNO_3$/HF system, can reduce the reflection of a wafer down to ~23%. In our preliminary works, the reflection loss of a DWS *mc*-Si wafer after the same texture process is still as high as ~28%, resulting in a 0.4% lower power conversion efficiency ($\eta$) than that of an MWSS wafer. Unlike the randomly and homogeneously fractured surface in MWSS wafers, the existence of directional saw marks and an incompletely covered amorphous Si layer in DWS wafers will result in an undesirable texture, as will be discussed later. Because *mc*-Si solar cells have occupied more than 80% of the photovoltaic (PV) market, it is an urgent requirement for PV researchers and the industry to develop an effective texture technique for efficient DWS *mc*-Si solar cells.

Recent progress in nanostructure textured black silicon has attracted intensive attention due to its great potential for applications in silicon-based solar cells [7–11]. There are several advantages of black silicon solar cells: excellent light trapping in a wide spectrum ranging from 300 to 2000 nm [7]; the possibility of removing the need for expensive plasma-enhanced-chemical-vapor-deposition (PECVD) processing; and wider acceptance angle of light [12]. There are three main types of techniques for fabricating black silicon: laser texturing [9,10], reactive ion etching (RIE) [13–16], and metal-catalyzed chemical etching (MCCE) [17,18]. For mass production, the RIE and MCCE techniques have high expectations, but obviously MCCE is much more suitable for the current industry product line where the texturing process is also based on chemical solutions due to their low-cost and stability. It is worth mentioning that the efficiency of the

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2017年，在Solar Energy Materials & Solar Cells发表论文，报道了湿法黑硅技术成功应用于类单晶硅太阳电池，并能获得具有优异陷光性能的倒金字塔结构，从而提升电池的效率。目前类单晶太阳电池已经进入规模生产阶段，同时验证了该低成本和全光谱陷光的倒金字塔绒面技术，有望应用于单晶硅太阳电池。

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# Efficient nanostructured quasi-single crystalline silicon solar cells by metal-catalyzed chemical etching

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ABSTRACT

Seed-assisted cast quasi-single crystalline silicon (Qsc-Si) technique allows the production of efficient, low-cost solar cells. However, most of the Qsc-Si wafers still consist of single- and multi-crystalline silicon grains, which lead to difficulties when attempting to achieve high efficiency by using conventional acid or alkali texture processes. This paper highlights the fact that nano-textured Qsc-Si solar cells can reach efficiencies ranging from 18.4% to 18.9% by using the same metal-catalyzed chemical etching technique, along with a depressed color difference. A parallel sub-cell model is proposed to explain how to enhance the performance of Qsc-Si cells.

## 1. Introduction

In recent years, crystalline silicon, including cast multi-crystalline (mc-Si), and Czochralski (CZ) single crystal (sc-Si), have dominated approximately 90% of the photovoltaic (PV) market [1–4]. From the viewpoint of the total cost of production, both sc-Si and mc-Si have advantages and disadvantages: costly sc-Si solar cells are efficient due to nearly perfect material quality, but suffer from serious light-induced degradation (LID) of efficiency due to B-O bonding; cost-effective mc-Si solar cells have 1–2% lower efficiencies than those of sc-Si cells because of more crystallographic defects and higher light loss [5–7].

The seed-assisted cast quasi-single crystalline silicon (Qsc-Si) technique was recently developed by carefully controlling the growth condition to grow < 100 > oriented sc-Si grains in most vertical and horizontal areas of an ingot [8–11]. Qsc-Si solar cells are expected to have efficiency close to that of sc-Si cells, due to high minority carrier lifetimes, lower grain boundaries and dislocations, while keeping the low cost and LID of mc-Si cells. It was reported that the efficiency of Qsc-Si solar cells has wide distribution, from 17.1% to 18.2%, as the ratio of sc-Si grains in the wafers varies from 50% to 100% [12–14]. However, Qsc-Si is still unpopular in the PV industry, due to two main factors: first, although it is higher in efficiency, the cost of Qsc-Si is higher than that of mc-Si. Second, most Qsc-Si wafers consist of both sc- and mc-Si grains, thus making it difficult to obtain proper texture for light trapping, and thus it reaches high efficiencies by using either conventional alkali or acid texture processes [15]. Therefore, the need to find an effective texturing technique for the efficient Qsc-Si cell is urgent.

The nanostructured black silicon with extremely low reflectivity has attracted attention due to its potential application in silicon-based solar cells [16,17]. Theoretically, the nano-texture can be treated as a density-graded or refraction-graded layer, which can smoothly connect the air and Si substrate, thus allowing it to suppress light reflection exponentially as the grade depth increases [18]. Several techniques, such as laser texturing, reactive ion etching (RIE), and metal-catalyzed chemical etching (MCCE), are attractive because various nanostructures can be formed on the surface regardless of grain orientations of Si wafers [19–24]. MCCE has been verified as a universal nano-texture technique for sc-Si and mc-Si wafers, and it is much more suitable for the current industry product line due to its low cost and stability. However, it is still a challenge to obtain a proper texture for both sc- and mc-Si grains in a Qsc-Si wafer, in an aim to achieve good cell performance, i.e., excellent light trapping ability, less color difference, and high efficiency.

In this work, the Qsc-Si solar cells with a mixture of sc- and mc-Si grains demonstrated 18.4% to 18.9% efficiencies using our well-established MCCE nano-texture process [25,26], and the results show that the cast Qsc-Si can be competitive with both CZ sc-Si and cast mc-Si.

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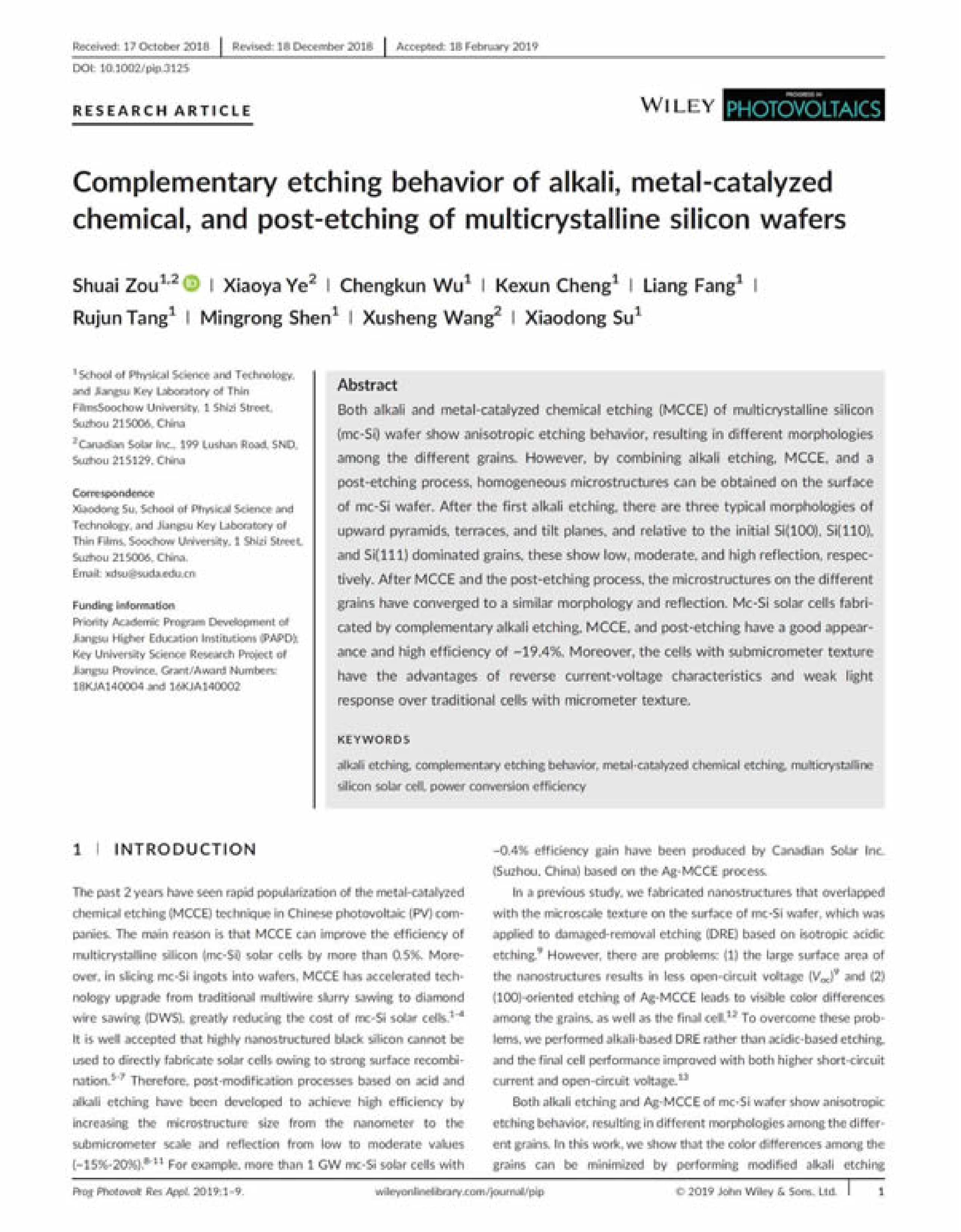
2019年，最新发表在Progress in Photovoltaics: Research and Applications的论文，提出了互补刻蚀的新机制，所制备的多晶黑硅电池外观均匀，并具有优异的电池/组件弱光响应以及较高发电功率。



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RESEARCH ARTICLE

WILEY PROGRESS IN PHOTOVOLTAICS

# Complementary etching behavior of alkali, metal-catalyzed chemical, and post-etching of multicrystalline silicon wafers

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## Abstract

Both alkali and metal-catalyzed chemical etching (MCCE) of multicrystalline silicon (mc-Si) wafer show anisotropic etching behavior, resulting in different morphologies among the different grains. However, by combining alkali etching, MCCE, and a post-etching process, homogeneous microstructures can be obtained on the surface of mc-Si wafer. After the first alkali etching, there are three typical morphologies of upward pyramids, terraces, and tilt planes, and relative to the initial Si(100), Si(110), and Si(111) dominated grains, these show low, moderate, and high reflection, respectively. After MCCE and the post-etching process, the microstructures on the different grains have converged to a similar morphology and reflection. Mc-Si solar cells fabricated by complementary alkali etching, MCCE, and post-etching have a good appearance and high efficiency of ~19.4%. Moreover, the cells with submicrometer texture have the advantages of reverse current-voltage characteristics and weak light response over traditional cells with micrometer texture.

KEYWORDS
alkali etching, complementary etching behavior, metal-catalyzed chemical etching, multicrystalline silicon solar cell, power conversion efficiency

## 1 | INTRODUCTION

The past 2 years have seen rapid popularization of the metal-catalyzed chemical etching (MCCE) technique in Chinese photovoltaic (PV) companies. The main reason is that MCCE can improve the efficiency of multicrystalline silicon (mc-Si) solar cells by more than 0.5%. Moreover, in slicing mc-Si ingots into wafers, MCCE has accelerated technology upgrade from traditional multiwire slurry sawing to diamond wire sawing (DWS), greatly reducing the cost of mc-Si solar cells.[1-4] It is well accepted that highly nanostructured black silicon cannot be used to directly fabricate solar cells owing to strong surface recombination.[5-7] Therefore, post-modification processes based on acid and alkali etching have been developed to achieve high efficiency by increasing the microstructure size from the nanometer to the submicrometer scale and reflection from low to moderate values (~15%-20%).[8-11] For example, more than 1 GW mc-Si solar cells with ~0.4% efficiency gain have been produced by Canadian Solar Inc. (Suzhou, China) based on the Ag-MCCE process.

In a previous study, we fabricated nanostructures that overlapped with the microscale texture on the surface of mc-Si wafer, which was applied to damaged-removal etching (DRE) based on isotropic acidic etching.[9] However, there are problems: (1) the large surface area of the nanostructures results in less open-circuit voltage ($V_{oc}$)[9] and (2) (100)-oriented etching of Ag-MCCE leads to visible color differences among the grains, as well as the final cell.[12] To overcome these problems, we performed alkali-based DRE rather than acidic-based etching, and the final cell performance improved with both higher short-circuit current and open-circuit voltage.[13]

Both alkali etching and Ag-MCCE of mc-Si wafer show anisotropic etching behavior, resulting in different morphologies among the different grains. In this work, we show that the color differences among the grains can be minimized by performing modified alkali etching

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