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Fabrication of seeded substrates for layer transferrable silicon films*

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The layer transfer process is one of the most promising methods for low-cost and highly-efficient solar cells, in which transferrable mono-crystalline silicon thin wafers or films can be produced directly from gaseous feed-stocks. In this work, we show an approach to preparing seeded substrates for layer-transferrable silicon films. The commercial silicon wafers are used as mother substrates, on which periodically patterned silicon rod arrays are fabricated, and all of the surfaces of the wafers and rods are sheathed by thermal silicon oxide. Thermal evaporated aluminum film is used to fill the gaps between the rods and as the stiff mask, while polymethyl methacrylate (PMMA) and photoresist are used as the soft mask to seal the gap between the filled aluminum and the rods. Under the joint resist of the stiff and soft masks, the oxide on the rod head is selectively removed by wet etching and the seed site is formed on the rod head. The seeded substrate is obtained after the removal of the masks. This joint mask technique will promote the endeavor of the exploration of mechanically stable, unlimitedly reusable substrates for the kerfless technology.

Keywords: seeded substrate, layer transfer, joint mask, filler, silicon film

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1. Introduction

The challenge of cost and efficiency is the main bottleneck for the current photovoltaic electricity to be commonly usable energy. In recent years, kerfless wafer technology has aroused great interest because it can produce mono-crystalline silicon wafers with flexible thickness directly from gaseous feedstock via a layer transfer process by reusable substrates.[1–6] This technology skipped off the traditional high energy consuming ingotting process and costly sawing process, thereby favoring the photovoltaic industry with cheaper wafers and less silicon crystal consumption. At the same time, the flexible and light-weighted cells are more available by the ready ultrathin wafers from this technology.

Among kinds of kerfless methods,[7–12] the technique based on double porous silicon has been most developed.[13–16] Up to now, the solar cells with an efficiency of 23% have been achieved and flexible solar cells with an efficiency of 21.2% have also been successfully made from this porous silicon kerfless technique.[17,18] However, this technique still faces some intractable problems for high crystalline quality and low cost, such as metal contaminants from the electrolyte during the formation of the porous bilayer, surface buckling during the recrystallization of the upper porous layer, and limited reuse of the mother substrates due to the inevitable re-building process of the porous bilayer, etc.[19–21]

Lately, our team developed the protruded-seed substrate technique for the kerfless technology with the endeavor of building an unlimitedly reusable substrate, getting rid of any recrystallization during epitaxial growth, and excluding metal contaminants from the structured substrates.[22,23] In our technique, silicon growth selectively started on the discretely distributed protruded seeds, neighborhoods were coalesced into integral films, and then the protruded supporting structures for the seeds evolved into a structured hollow between the grown films and the mother substrates, providing the grown films with the capability of detachment and transfer. In our previous efforts,[23] we used molten wax to fill the space between the rod arrays, thereby forming a wet-etching resist mask for selective removal of the oxide layer on the rod head, thus the rod heads were selectively chosen as the seed sites. However, because the filming property of wax was not good enough to perform uniform thin coating, the wax filling method is not suitable for the case where shorter rods are used as the seed supporting structure. Additionally, it was found there were always some tough stained spots on the prepared substrates, which may result from the undefined chemical reactions between the buffered oxide etchant (BOE) solution and the wax resist mask. In order to improve the mechanical stability, i.e., the process tolerance of seeded structures, such as wet-cleaning, drying, stripping, etc., shorter rods are more desir-

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able for the fabrication of protruded seed structures. Hence, it is necessary to explore another route to fabricating the protruded seeded substrates by new masking material with the properties of high film uniformity and flatness, and easy removal. In this work, we demonstrate our progress of this concerning aspect.

2. Experiment

2.1. Fabrication of silicon rod arrays

The periodically patterned silicon rod array was prepared through the photolithography and inductive coupled plasma (ICP) dry etching on Czochralski mono-crystal silicon (Cz-Si) wafers. Typically, the rods each had a diameter of 4 μm and length of 10 μm, while the array had a period of 10 μm. Thermal oxidization was used to form a SiO_2 sheath layer on the wafer and rods, and the typical thickness of oxide layer was 350 nm.

2.2. Preparation of filled mask using the photoresist

The photoresist was a traditional etching resist material in the semiconductor industry, and its flat and thin films can be easily obtained by spin-coating. In our experiments, the photoresist was also employed to fill the space between the rods by spin-coating and to form an effective resist mask for the rod sidewalls under the later wet-etching process. The photoresist from the Suzhou Ruihong Electronic Chemical Co., LTD, RZJ-304–25CP was used originally. The spin-coating was performed under 1000 rpm–3000 rpm, and then the coated films were cured and dried in an oven at 60 °C–80 °C.

2.3. Preparation of joint resist mask by evaporated aluminum film, lightly coated photoresist, and PMMA

Thermal evaporation is a usual method of depositing uniform films with large areas. Usually, the aluminum can be deposited by evaporation at a speed of more than 20 Å/s, so several microns thick aluminum films should be easily obtained by this deposition method. From these points, evaporated aluminum is a good choice for preparing the filled mask among the rods. In our experiments, the evaporation was performed under 1.0×10^{-3} Pa pressure, and was split into several durations in order to avoid overheating the chamber. The deposited aluminum films were typically 5 μm–7 μm thick.

In general, the aluminum deposition simultaneously happened in the space between the rods and on the heads of the rods. In order to unveil the rod head for the next selective removal of the oxide on the heads, the deposited aluminum on the rod heads should be removed. After the deposition of aluminum on the rod arrays, the 1:10 diluted photoresist by hexane was spin-coated on the aluminum film, then a mild oxygen plasma was used to etch off the part of the photoresist film from the rod head aluminum. Subsequently, the aluminum layer on the heads of the rods was removed by the mixed solution (volume ratio) of 80% H_3PO_4 (85%), 5% H_3NO_4, 5% CH_3COOH, and 10% H_2O at 50 °C. Because of the side etching effect, when the aluminum on the rod heads was wet-etched, etching also happened down along the rods to form gaps between the rod and the remaining aluminum film. PMMA films were spin-coated on the etched aluminum film, and used to stuff the gaps formed by the side-etching, between the rods and the remaining aluminum film. The PMMA solution is 92 mg/ml in chlorobenzene. After being PMMA spin-coated, the substrate was kept at 60 °C for 2 h and 160 °C for 12 h to completely stuff the above-mentioned gap with PMMA films. When the substrate was cooled down to room temperature, a thin layer of photoresist (1:10, hexane diluted) was spin-coated at 3000 rpm on the ready PMMA film, which was used to protect the PMMA film from later wet-etching BOE.

2.4. Preparation of seeded substrates by selectively wet-etching

When the joint mask was ready, the mild oxygen plasma was again applied to the substrate, and the thin layer of PMMA and photoresist on the rod heads was removed. Then the substrate was placed into a BOE solution ($HF:NH_4F = 1:6$) and kept there for 5 min–10 min, thus the oxide layer on the rod heads was selectively removed. In the following, the PMMA and photoresist film were dissolved off by acetone solvent and the residual aluminum was removed by the mentioned mixed solution for its wet-etching. After being fully rinsed and washed by DI water, and dried by nitrogen purge, the protruded seeded substrate was developed.

2.5. Characterization of morphologies

The morphologies of the samples were characterized by a scanning electronic microscope (Hitachi S-3400 N) and an optical microscope (OM, Keyence, VK-9710, colored three-dimensional laser scanning microscope).

3. Results and discussion

Figure 1 shows the optical microscopic morphologic image of the rod array on the wafer substrate spin-coated with photoresist. The picture reveals that the spin-coated photoresist cannot completely fill the space between the rods. In our further experiments (not shown here), it was also found that gaps always existed between the rod and the filled photoresist, regardless of the periods of the rod patterns and the times of spin-coating. We think that the photoresist glue is not well adhesive to the silicon oxide surface, resulting in the separation of the coated photoresist from the side surfaces of the rods when the solvent in the glue is volatilized by spinning and the glue became shrunk and dried, thus the gaps appear. If the coated photoresist is not masked, the oxide layer on the

sidewalls of the rods will also be removed in the next BOE wet-etching process. Therefore, it is not feasible that the photoresist filled mask is prepared just by spin-coating. In order to improve the adhesiveness of the photoresist to the sidewalls of the rods, hexamethyldisiloxane (HMDS) molecules have also been used to modify the oxide surface of the wafer substrate and the rods, then the photoresist is spin-coated. Certainly, the gaps between the coated photoresist and the sidewall of the rod become disappeared (images not shown here). However, we gave up the approach of using a photoresist to prepare the filled mask for selective removal of the oxide layer on the rod heads, based on the following experimental phenomena. Multiple spin-coating is indispensible for a thick filled photoresist: on the one hand, the filled photoresist is much thicker on the margin area than on the center area of the substrate due to the blocking effect of the rod array; on the other hand, this thickness nonuniformity would increase with the times of spin-coating. The coated photoresist on the rod head is too thick, so long duration of oxygen plasma etching is necessary to get gid of it; this kind of plasma etching breaks the bonding of the filled photoresist with the sidewall of the rods, thus the filled phohoresist does not work as the wet-etching-resist mask for the sidewall of the rods.

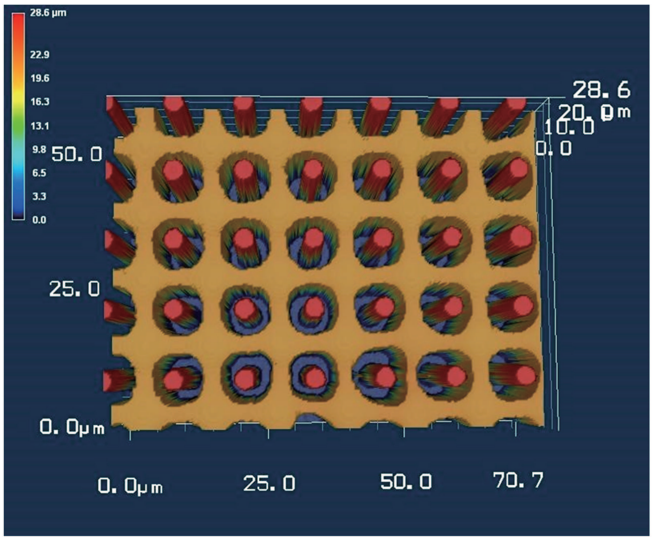


Fig. 1. (color online) Optical microscopic image of rod arrays spin-coated with photoresist.

Actually, a thin layer of photoresist (less than 1 micron in thickness) can act as a good wet-etching resist mask for the layer below the oxide layer. If the photoresist filler between the rods is largely replaced by some insoluble stiff materials and only a few resist materials (such as photoresist, PMMA) need to be inserted between the stiff material and the rods to provide the wet-etching mask function for the sidewall of the rods, this kind of polymer insertion could be performed by single spin-coating using well-diluted glues or low-concentrated solution. In this way, the blocking effect of the rod array can be excluded for the spin-coating and uniform coating across a large area becomes practical; the coating on the rod head is very thin and could be easily removed by a short-time mild oxygen plasma etching. In our experiments, the evaporation-deposited aluminum acts as the insoluble stiff filler between the rods.

The morphological contrast of the rod array before and after the aluminum deposition is demonstrated in Fig. 2. Obviously, not only the deposition happened in the space between the rods, but also much aluminum is deposited on the rod head, forming a bigger diameter pillar. The deposited aluminum particles have rather big sizes and present a rough surface since the evaporation is performed at a well high rate of more than 20 Å/s. At the same time, the bigger diameter of the aluminum pillar than that of the original rod and the nonplanar head of the pillar indicates that the deposition under 10^{-3} Pa vacuum level is not well directional, and lateral deposition also partly happens. Now that the aluminum pillar deposited on the rod head has a growing diameter with the deposition going on, the pillar will bring about a shielding effect for the deposition near around the rod, resulting in the fact that the filling close around the rod would not be done well. This shielding effect can be overcome by enhancing the chamber vacuum level and reducing the evaporation rate, but a low evaporation rate is unaffordable and time-consuming for thick film deposition. Anyhow, this shielding effect does not seem to exert a negative influence on the next role of the deposited aluminum as the stiff filler.

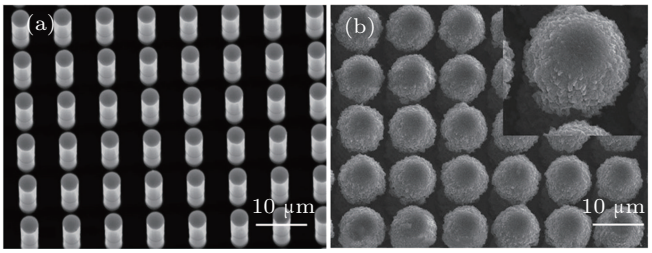


Fig. 2. Morphological contrast of the rod arrays (a) before and (b) after aluminum deposition by thermal evaporation.

The etching of aluminum pillars on the rod heads was shown in Fig. 3, revealing that the pillars on the rods can be completely removed while the filled aluminum between the rods is mostly preserved. As expected, it can be found that there are gaps between the rods and the remaining aluminum filler, and the gap distance increases with the etching duration increasing. Thus it can be inferred that the thin layer of photoresist coating by well-diluted photoresist glue provides well adequate etch-resist for the deposited aluminum between the rods, and the aluminum etching starts from the pillars and then comes down along the rods, leaving behind gaps between the rods and the remaining aluminum filler. Meanwhile, the photoresit coated on the pillars should suffer much severer oxygen plasma etching than that coated on the deposited aluminum between the rods because of the tipping effect, like this, it could be expected that when the photoreist is fully etched off on the

aluminum pillars, much photoresist still remains on the surface between the rods, this left photoresist prevented its below aluminum film from being etched when the aluminum pillars are etched away.

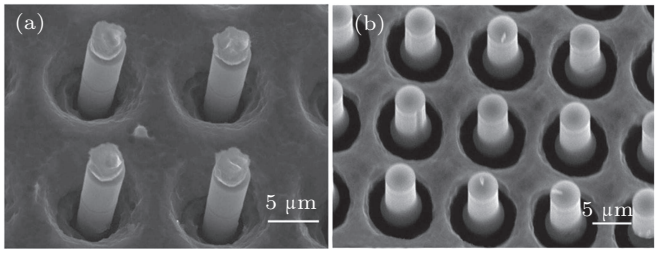


Fig. 3. SEM images displayed removal of the aluminum pillars on the rod heads by different wet-etching durations: (a) 8 min and (b) 10 min.

After the aluminum pillars are removed from the rod heads, PMMA is spin-coated to stuff the gaps between the rods and the remaining aluminum film, and a thin layer of photoresist is then coated on the cured and dried PMMA film; eventually, the joint resist mask for the selective removal of the rod head oxide layer by BOE solution comes into being.

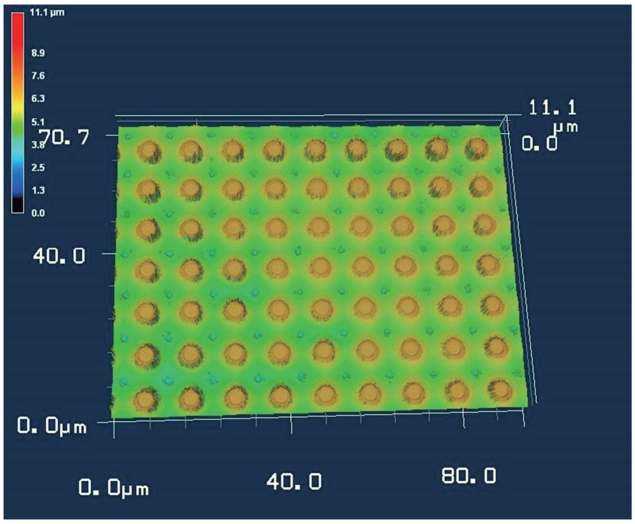


Fig. 4. (color online) Optical-microscopic morphologic image of joint mask, showing gaps between rods and left aluminum film were fully stuffed while rods shoot up from the mask.

Figure 4 demonstrates the morphology of the joint mask. Clearly, the gaps around the rods disappear and the filled mask is seamlessly linked up with the rod sidewall while some parts of the rod shoot up from the mask. We find that, in order to ensure the gaps around the rods are absolutely fully filled, it is a key step that the coated PMMA should be kept at a high temperature for a long time (160 °C and 12 h are adopted in our experiments). Since the PMMA polymer transforms from solid phase to liquid phase at 140 °C–220 °C, when the filled PMMA is held at 160 °C, it gradually turns into liquid phase and seeps down along the rods to push out some random voids. In this way, the gaps around the rods are fully filled and the filled PMMA is tightly bonded to the sidewalls of the rods. In our experiments, the photoresist has also tried to stuff the gaps around the rods, but it is not a good option due to the following two facts: the filled photoresist cannot become melted to refill the gaps, and it cannot function as the resist mask for the oxide surface during the next BOE etching when it has suffered the influence of oxygen plasma, maybe becomes exposed and fails to bond to the oxide surface.

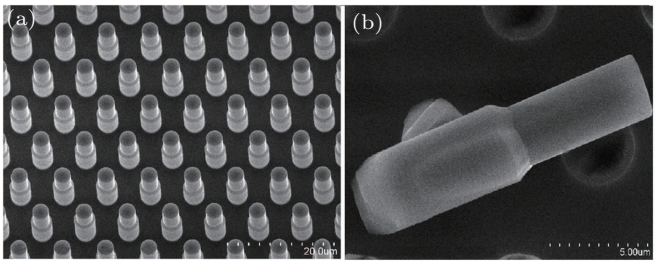


Fig. 5. SEM images of rods with the oxide layer selectively removed from the head, revealing seeded substrate achieved, (a) full-view of the seeded rod array and (b) a single seeded rod by scratching down.

After the masked substrate undergoes a short mild oxygen plasma to remove the thin layer of PMMA and photoresist from the rod heads, BOE etching is performed on the substrate to selectively remove the oxide layer from the rod heads. When the joint mask is removed, the expected seeded substrate can then be seen. Figure 5 exhibits the obtained protruded seeded substrate. Evidently, the oxide layer on the rod head is uniformly removed and the silicon core of the rod comes out on the head part, forming a seeded site where once silicon epitaxial growth is performed, preferred growth starts while no growth takes place on the oxide surface.[23] A broken rod is shown in Fig. 5(b), indicating the naked silicon core is about 5-μm long, i.e., the residual oxide layer on the rod is still 5-μm long, almost equivalent to the thickness of the filled aluminum film. This case proves the joint mask performs well as the BOE etching-resist for the selective removal of the oxide layer on the rod heads. If the length of naked silicon core is shorter, thicker aluminum films should be deposited. The energy dispersive x-ray (EDX) spectrum of the seed head is shown in Fig. 6, indicating that the oxygen content of the head is less than 4%, further demonstrating that the oxide layer on the rod head is entirely selectively removed. The success of the joint mask for BOE selective-etching resist can be attributed to being due to the following advantages. The filled aluminum film is comprised of isolated micro-pools around the rods, and the isolated micro-pools can confine PMMA solution around the rods to achieve well thick PMMA filled there even if the filled PMMA is spin-coated by low concentrated solution. The PMMA polymer can become melted at below 200 °C, which makes it certain that the gaps between the rods and the remaining aluminum film are fully stuffed and the polymer is tightly bonded to the sidewalls of the rods. Further, the diluted

and low-concentrated polymer glue is applicable for the joint mask construction, which ensures that the uniform spin-coated polymer film across a large area on the structured surface and short mild oxygen plasma processing work well to remove the polymer from the rod heads. Also, the photoresist can exclude the damage from the BOE solution on the PMMA film even though it is affected by the plasma.

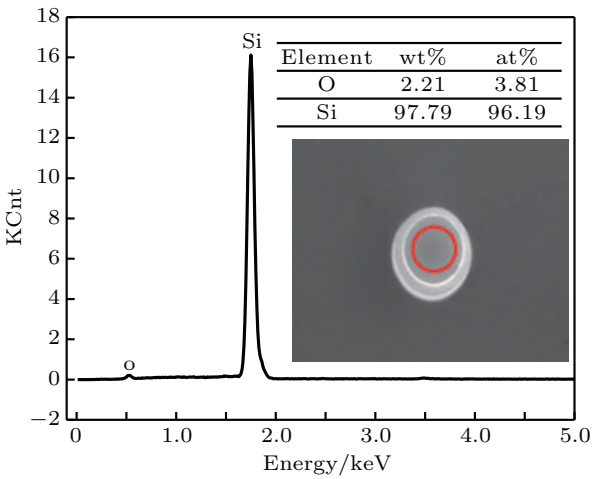


Fig. 6. (color online) EDX spectrum of rod head after the oxide layer has been selectively removed. Inset shows the SEM image of the seed rod and element content.

4. Conclusions

In this work, we have displayed the progress of the fabrication of protruded seeded substrates for the layer-transfer kerfless silicon wafer/film technology by using the traditional spin-coating, thermal evaporation, wet-etching, and oxygen plasma etching techniques. It is found that during the course of transforming rod patterned substrates into the seeded substrates, the filled mask for selective head etching cannot be built just by spin-coating photoresist or other polymer glues mostly because of the challenge of the uniform coating on rod patterned substrates. The deposited aluminum films by thermal evaporation are used to form isolated micro-pools around the rods for confining the coated glue or solution, then the joint mask is realized by the residual aluminum film, spin-coated PMMA and photoresist, and the non-uniformity of the coated polymer across the substrate is overcome by using a low-concentrated solution or well-diluted glue. At the same time, the coated polymer layer on the rod head is very thin and a short mild oxygen plasma does well to remove it. The obtained joint mask performs well to selectively remove the oxide layer from the rod heads under BOE solution, and protruded seeded substrates are achieved with uniform seed parts on the rods. The joint mask technique will promote our endeavor of the exploration of mechanically stable, unlimitedly reusable substrates for the kerfless technology.

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