# High-strength nanostructured black-silicon wafer for photovoltaic applications

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Published in Micro & Nano Letters; Received on 18th August 2016; Accepted on 25th August 2016

Silicon nanostructures can improve the bending strength of wafers, but often trap particle contaminates. A double-sided surface nanostructure with a morphology controlled via wet chemical etching is used to both improve the mechanical strength and reduce surface reflection. Compared with a conventional polished silicon wafer, the bending strength was increased by 3.4 times and the surface reflection was reduced to 1%, and so can provide a promising solution for photovoltaic applications. The optically unused side of the wafer was protected by a thin silicon layer that prevented the entrapment of particles that might cause glitches in subsequent fabrication processes, all the while maintaining the enhancement in strength. The particle test confirmed that incorporating protection layer intacts the particle count with polished silicon sample.

**1. Introduction:** The unique electrical and mechanical properties of silicon wafers have seen them widely used in industry [1], but a brittleness caused by microdefects in their surface can often lead to catastrophic fracture [2]. These microdefects are typically introduced during manufacturing processes such as grinding [3] and polishing [4] and represent a major hurdle to improve the strength of silicon wafers. Strength improvement techniques that currently exist include dopant diffusion [5], defect size reduction [4] and crack deflection [6], but these all affect the bulk properties of the material.

Surface nanostructure strengthening is a relatively new method for improving brittle materials while retaining their bulk properties [7]. Silicon nanostructures are widely used in semiconductor, photovoltaic (PV) and bio-medical applications [8, 9]. Silicon nanostructures used in PV applications are either focusing on improving bending strength or acting as an antireflective coating for better light absorption [10, 11]. Silicon nanostructures can also be used to strengthen rollable integrated circuits (ICs) [12], but the entrapment of particles between nanostructures [13] can affect the electrical and mechanical properties of the device, as well as subsequent fabrication processes, to the extent that device failure can occur [14].

The current Letter presents a solution for simultaneously achieving higher strength and lower surface reflection from silicon wafers using surface nanostructures by covering the optically unused surface with a protective layer to prevent particle trapping. As both the front and back of a silicon wafer contain unavoidable randomly distributed microdefects that affect the mechanical strength of PV or IC devices [15], nanostructures were fabricated on both sides of the wafer to mitigate against their strength degrading effect. The morphology of these nanostructures was controlled so as to achieve both an enhancement in strength and a sufficient reduction in light reflection to produce black-silicon wafers. As only a single wafer surface was needed to absorb light, the optically unused nanostructured side was protected by a thin silicon layer. This prevents particles being trapped within the gap between adjacent nanostructures, but still maintains the enhanced bending strength compared with a non-protected nanostructured silicon wafer. It also helps to prevent the silicon nanostructures being damaged during subsequent processing steps.

**2. Fabrication and testing:** Silicon nanostructures were fabricated using metal-assisted wet chemical etching process. The silver (Ag) particle was deposited which act as noble metal catalyst. The oxidising agent oxidises the silicon to silicon dioxide beneath the noble metal which was further etched away by dissolving in hydrofluoric acid (HF) at noble metal and solution interface [16]. The aqueous solution consists of 0.01 M Ag nitrate, HF (49 wt%) and hydrogen peroxide ($H_2O_2$) (30 wt%) was used to fabricate silicon nanostructures as shown in Fig. 1*a*. The as-fabricated nanostructures had an irregular etching depth because of aggressive etching rate of 1 μm/min, which resulted in a non-uniform base nanostructure that can reduce the strength of the silicon wafer by concentrating the stress at irregularities [7].

The wet chemical etching method was therefore modified by removing the strong oxidising agent ($H_2O_2$) from the etchant to form the uniform silicon dioxide beneath the Ag particle. The etching rate was reduced from 1 to 0.1 μm/min. Though the etch rate of this metal-assisted etching approach is slower, it produced nanostructures with a more regular depth profile than the first recipe, as shown by the tilted-view scanning electron microscopy (SEM) images in Fig. 1*b*. The top-view SEM images in Fig. 1 also confirm that the nanostructure fabricated without a strong oxidising agent has more uniform thickness than the nanostructure fabricated with a strong oxidising agent. Both nanostructure types were subsequently immersed in nitric acid (70%) solution to dissolve the Ag particles, and then a thin layer of silicon was deposited by chemical vapour deposition. Finally, this protective layer of silicon was polished by chemical mechanical polishing (CMP).

To evaluate what significance the uniformity of the nanostructure base has, the room-temperature bending strength of both nanostructure types was estimated from a three-point bending test using (1) [17]. For this, the samples were placed into material testing machine (Hung Ta HT-2102A) with a 980-N load cell (Hung Ta 8336)



doi: 10.1049/mnl.2016.0533

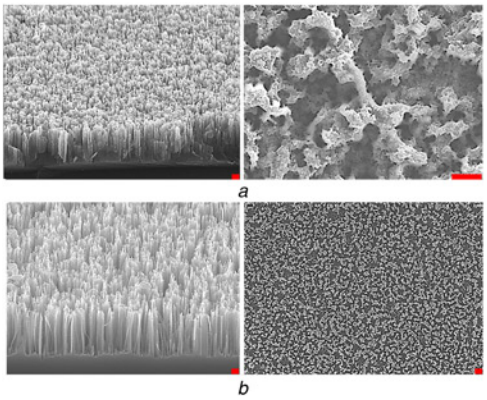


**Fig. 1** *Tilted- and top-view SEM images of*
*a* Non-uniform
*b* Uniform base nanostructures (all scale bars are 500 nm)

$$\sigma_{br} = \frac{1.5F_r L}{wt^2} \quad (1)$$

where $F_r$, $L$, $w$ and $t$ are the load at rupture, span length, width and thickness of the sample, respectively.

The optical properties of a silicon wafer are known to be improved by surface nanostructures [18], which can enhance light absorption by reducing surface reflection. The surface reflection of the uniform base nanostructures was therefore measured in the 400–1000 nm range using a ultraviolet (UV)–vis–near infra red (NIR) spectrophotometer (U4001, Hitachi Inc.) equipped with an integrating sphere at a fixed incident angle of 5°.

**3. Result and discussion:** The bending strength of the non-uniform base nanostructure was measured with different depths of 500 nm, 1 µm, 1.5 µm, 2 µm, 2.5 µm, 3 µm and 3.5 µm. In Fig. 2*a*, the maximum bending strength was with a depth of 1.5 µm, which represented a two-and-a-half-fold increase (0.25–0.62 GPa). Any subsequent increase in nanostructure depth, however, led to a decrease in bending strength due to the irregular etching depth generating non-uniform stress near irregularities [7]. That is, these areas of irregular depth can act as crack initiation points that cause the sample to break at a lesser force.

The bending strength of the uniform base nanostructures was measured for samples with nanostructure depths of 1, 2, 3, 4, 6 and 8 µm. As shown in Fig. 2*b*, this found that the bending strength increased three-and-a-half-fold (from 0.25 to 0.88 GPa) and saturated at a depth of 4 µm. As this is a greater strength improvement than was achieved with the non-uniform base nanostructure, a uniform base nanostructure is considered a more suitable candidate for practical application.

As shown in Fig. 3*a*, the average surface reflection of the polished silicon sample was measured as 40%. The reflectivity of uniform nanostructure sample decreased with increasing depth, reaching a minimum of 1% at a depth of 4 µm. This reduced surface reflection is indicative of higher absorption in the silicon wafer; i.e. a black-silicon wafer (Fig. 3*b*) suitable for PV applications.

Using a double-sided nanostructure can not only reduce the strength degrading effect of microdefects on both sides of the wafer, but also improve the optical performance of both sides. However, double side optical performance is not important in every application. Thus, in applications in which single side optical performance enhancement is sufficient, or optical improvement is not required, the nanostructures of optically unused side can be protected using a thin layer of a suitable material deposited on top of the fabricated nanostructure. In this Letter, nanostructures were protected by thin layer of silicon, and after polishing this protection layer surface reflection was nearly same as polished silicon sample. Thus, this side of protected wafer can only improve the bending strength without affecting the optical properties. This can reduce the risk of failures caused by particles being trapped between nanostructures, and so for this Letter, a silicon layer was used to ensure compatibility with current PV and IC technology (Fig. 4).

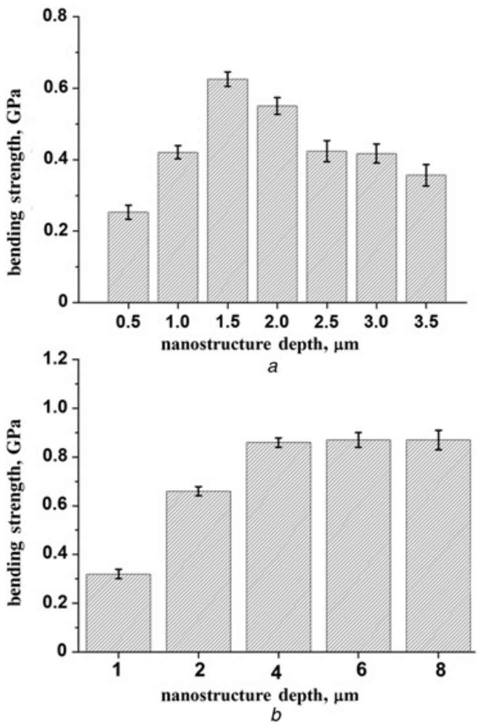


**Fig. 2** *Bending strength of different depths*
*a* Uniform
*b* Non-uniform nanostructures, as evaluated by a three-point bending test

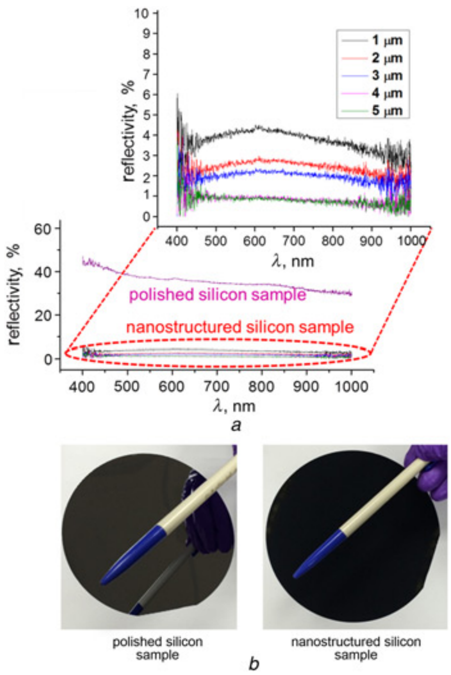


**Fig. 3** *Average surface reflection of the polished silicon sample*
*a* Reflection of uniform base nanostructures with different depths
*b* Polished and nanostructured (black) silicon

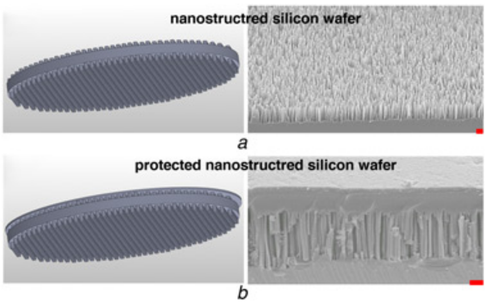


**Fig. 4** *Compatibility with current PV and IC technology*
*a* Schematic and SEM for (a) nanostructure fabrication on both sides
*b* Silicon layer protection after nanostructure fabrication (all scale bars are 500 nm)

As shown in Fig. 5*a*, the bending strength of the silicon wafer increased from 0.25 to 0.84 GPa after nanostructure fabrication, but decreased to just 0.82 GPa after deposition of the protective layer.

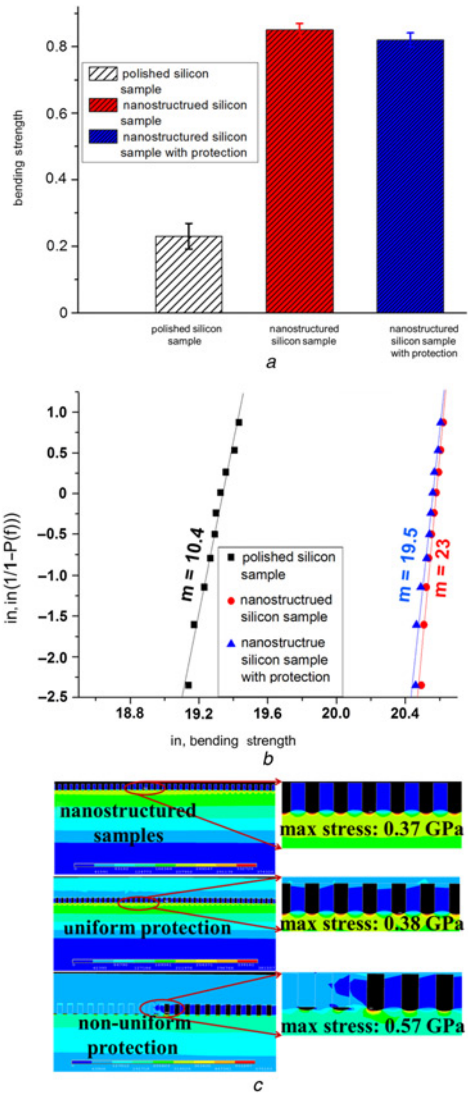


**Fig. 5** *Bending strength of the silicon wafer*
*a* Three-point bending strength
*b* Weibull analysis of polished silicon, nanostructured silicon and protected nanostructured silicon
*c* Simulation results for nanostructured silicon: nanostructured silicon with a uniform protection layer and nanostructured silicon with a non-uniform protection layer

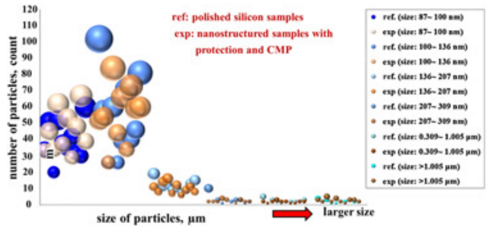


**Fig. 6** *Comparison of particle counts between polished silicon and protected nanostructured silicon samples*

The fact that this value is very close to that of the non-protected nanostructure confirms that this is a valid protection method.

The reliability of the protected surface nanostructure strengthening method was evaluated from the Weibull modulus ($m$) obtained from statistical variations in the bending strength of nearly identical samples under the same testing conditions, which is related to bending strength and failure probability [19]. As shown in Fig. 5*b*, the value of $m$ for the polished silicon, nanostructured silicon and protected silicon was found to be 10.4, 23 and 19.5, respectively. As the strength degrading effect of pre-existing randomly distributed defects in polished silicon causes a large deviation in the bending strength, the higher $m$ values of the nanostructured and protected nanostructured samples further confirm the usability and reliability of this method.

While a protective layer for nanostructures can help prevent contamination by foreign particles, a uniform surface is very important to improve the bending strength. Thus, any non-uniformity arising from irregular deposition of the protective layer will reduce the bending strength through increased stress concentration. To confirm this, the stress distribution of uniform and non-uniform protection layers was examined through mechanical simulation using ANSYS 12.1 (finite element analysis) software. As shown in Fig. 5*c*, maximum stress (0.37 GPa) occurs at the bottom of the nanostructure, but this is effectively the same as the maximum stress with a uniform protective layer (0.38 GPa). Moreover, the distribution of stress in the uniformly protected and non-protected nanostructures is similar. Non-uniform deposition of the protective layer, however, increased the maximum stress by 50% (from 0.37 to 0.57 GPa), with maximum stress occurring at discontinuities created by the non-uniform deposition. This increase in stress confirms that uniform deposition of the silicon protection layer is needed to ensure uniform stress distribution.

Particle testing was performed to identify the presence of any unwanted particles on the polished sample and nanostructured sample with protection, but as shown in Fig. 6, the number of particles on both samples was much the same. As the chance of trapping a smaller particle is higher due to their greater ability to get between nanostructures, the equal number of smaller particles suggests an absence of foreign particle contamination.

**4. Conclusion:** This method for producing a double-sided nanostructure presented here provides a new way to simultaneously improve both the bending strength and optical properties of a silicon wafer by controlling the nanostructure morphology. With a uniform base nanostructured surface, the bending strength was increased three-and-a-half-fold (0.25–0.88 GPa), whereas a two-and-a-half-fold increase (0.25–0.62 GPa) was all that could be achieved with a non-uniform base nanostructure. The surface reflection of the uniform base nanostructure was reduced to just 1%. A higher value of $m$ (19.5) for the protected nanostructured silicon compared with polished silicon (10.4) confirmed the reliability of this method. Protecting the optically unused nanostructured surface prevents particle contamination of the wafer without affecting its bending strength.



doi: 10.1049/mnl.2016.0533

Mechanical simulation demonstrated that a non-uniform protection layer can increase the maximum stress by 50% (from 0.37 to 0.57 GPa) through a reduction in deposition depth irregularity within the nanostructure, which leads to a less uniform stress distribution. This confirmed the importance of ensuring a uniform protection layer to maximise the improvement in strength. As the number of particles on the polished and protected nanostructured samples was the same, indicating that there was no entrapment of contaminants. This method presents a new way of fabricating improved black-silicon wafers for PV and IC applications.

**5. Acknowledgments:** This work was partly supported by the Ministry of Science and Technology, Taiwan (MOST) through project 104-2622-E-007-008-CC2. The authors are also grateful for the research support provided by the Instrument Technology Research Center (ITRC) for measuring the optical characteristics.

## 6 References

[1] Petersen K.E.: 'Silicon as a mechanical material', *Proc. IEEE*, 1982, **70**, pp. 420–457

[2] Connally J.A., Brown S.B.: 'Slow crack-growth in single-crystal silicon', *Science*, 1992, **256**, pp. 1537–1539

[3] Pei Z.J., Fisher G.R., Liu J.: 'Grinding of silicon wafers: a review from historical perspectives', *Int. J. Mach. Tools Manuf.*, 2008, **48**, pp. 1297–1307

[4] Nanz G., Camilletti L.E.: 'Modeling of chemical–mechanical polishing – a review', *IEEE Trans. Semicond. Manuf.*, 1995, **8**, pp. 382–389

[5] Hu S.M.: 'Dislocation pinning effect of oxygen-atoms in silicon', *Appl. Phys. Lett.*, 1977, **31**, pp. 53–55

[6] Kermode J.R., Ben-Bashat L., Atrash F., *ET AL.*: 'Macroscopic scattering of cracks initiated at single impurity atoms', *Nat. Commun.*, 2013, **4**, pp. 1–8

[7] Kashyap K., Kumar A., Huang C.T., *ET AL.*: 'Elimination of strength degrading effects caused by surface microdefect: a prevention achieved by silicon nanotexturing to avoid catastrophic brittle fracture', *Sci. Rep. UK*, 2015, **5**, pp. 1–13

[8] Gabrielli L.H., Cardenas J., Poitras C.B., *ET AL.*: 'Silicon nanostructure cloak operating at optical frequencies', *Nat. Photonics*, 2009, **3**, pp. 461–463

[9] Santos H.A., Hirvonen J.: 'Nanostructured porous silicon materials: potential candidates for improving drug delivery', *Nanomed. UK*, 2012, **7**, pp. 1281–1284

[10] Oh J., Yuan H.-C., Branz H.M.: 'An 18.2%-efficient black-silicon solar cell achieved through control of carrier recombination in nanostructures', *Nat. Nanotechnol.*, 2012, **7**, pp. 743–748

[11] Garnett E., Yang P.: 'Light trapping in silicon nanowire solar cells', *Nano Lett.*, 2010, **10**, pp. 1082–1087

[12] Kashyap K., Zheng L.C., Lai D.Y., *ET AL.*: 'Rollable silicon IC wafers achieved by backside nanotexturing', *IEEE Electron Device Lett.*, 2015, **36**, pp. 829–831

[13] Qin K.D., Li Y.C.: 'Mechanisms of particle removal from silicon wafer surface in wet chemical cleaning process', *J. Colloid Interface Sci.*, 2003, **261**, pp. 569–574

[14] Kamo T., Terasawa T., Yamane T., *ET AL.*: 'Evaluation of extreme ultraviolet mask defect using blank inspection, patterned mask inspection, and wafer inspection', *J. Micro-Nanolithogr. MEMS*, 2011, **10**

[15] Jiang A.L.X., Ming L.C., Gao J.C.Y., *ET AL.*: 'Silicon wafer backside thinning with mechanical and chemical method for better mechanical property'. IEEE, 2006, pp. 1–4

[16] Huang Z.P., Geyer N., Werner P., *ET AL.*: 'Metal-assisted chemical etching of silicon: a review', *Adv. Mater.*, 2011, **23**, pp. 285–308

[17] 'Standard test methods for bend testing of metallic flat materials for spring applications involving static loading'. ASTM E855, 2013

[18] Hsieh C.M., Chyan J., Hsu W.-C., *ET AL.*: 'Fabrication of wafer-level antireflective structures in optoelectronic applications'. IEEE, 2007, pp. 185–186

[19] Klein C.A.: 'Characteristic strength, Weibull modulus, and failure probability of fused silica glass', *Opt. Eng.*, 2009, **48**, pp. 113401-01–113401-10