THE HISTORY OF "BLACK SILICON" IN PHOTODETECTOR PATENTS

Leonard Forbes*, Life Member IEEE
L. Forbes and Associates, LLC
PO Box 1716
Corvallis, OR 97339
lenforbes@forbes4.com

"Black silicon" is a semiconductor material, a surface modification of silicon with very low reflectance of visible and infrared light. The modification was discovered in the 1960's as an unwanted side effect of chemical etching[1] and again in the 1980's as an unwanted side effect of reactive ion etching.[2] Black silicon, or textured surfaces, can be inadvertently produced by any of a number of known chemical etches, and are to be avoided in integrated circuits. [3]

Unfortunately in the late 1990's and 2000's black silicon was again produced as an effect of laser ablation and etching and consequentially some magical photoelectric properties were claimed by Prof. Eric Mazur and his students a Harvard University. One of the best examples of this is the 2006 paper by J.E. Carey et al. claiming a very high photo-gain associated with "the high density of impurities and structural defects in the microstructured layer." [4] It turns out in retrospect that the high gain was probably associated with a bulk silicon photoconductive effect as a result of annealing the high resistivity float zone, FZ, silicon substrates at 700C to 800C resulting in conversion of the substrate to even higher resistivities by the introduction of oxygen donors. By their own admission there was a long period of time they could not duplicate the photodetector effects, presumably they had unknowingly changed to Czochralski, CZ , substrates that are lower resistivity and for which it is more difficult to form high resistivity substrates. All the results in their journal article [4] can be explained as photoconductors on high resistivity bulk silicon substrates with poor contacts. Photoconductors can have a very high photogain. [6] The Harvard University and SiOnyx 2009 patent application [5] claimed a "photovoltaic effect" as well as the "high gain photodiodes." Fig. 13 in their report supposedly demonstrating this photovoltaic effect has no photovoltage at zero current! By definition "photovoltaic" means some photovoltage develops under illumination of an open circuit connected semiconductor junction diode. It is also difficult to have "high gain photodiodes" unless you have some mechanism for carrier multiplication, but it is fairly easy to have high gain photoconductors [6], or even negative photoconductivity [7] !

Nature has been using the textured structures technology for probably millions of years. A moth's eye has pillars on the surface of the eye, a texture, that reduces reflectance to one or two per cent. [8] In the case of tropical butterflies mother nature is even more clever, the textured surface on their wings reflects polarized light that only other butterflies can see, to predators the butterfly is a green against a green background.[9] The first human reference describing the textured structure and reduced reflectance as applicable to moths and applicable to solar cells is probably in 1935 by Von D. A. G. Bruggemann.[10] He described one mechanism for reduced reflectance, a lowering of the average index of refraction making possible the use of antireflecting layers, partly of silicon, partly of air. Antireflecting layers with a lower index of refraction than glass are commonly used in eye glasses. Another effect to reduce reflection on solar cells was a large pyramid texture resulting in multiple attempts at transmission into the silicon. Front side texturing of photodetectors to reduce reflectance and increase the scattering of light in the substrate was described by Arndt et al. of COMSAT in 1975. [11] Arndt described both the use of front side texture and antireflecting layers.

Backside textured surfaces for photdetectors were first described in the 1960's. A.E. St. John described backside texturing of photodetectors in 1969[12] and these were again described in 1983 by Czubatyj et al. [13]. A.E. St John suggested a simple formulation for the enhancement of the absorption of weakly absorbed infrared light in silicon by the scattering of this light at the textured backside and increased path length for absorption. We just adapted and modified this using a simple assumption in our review article and analysis of solar cells.[14] Different textures for solar cells were widely investigated in the early 1980's particularly by Yablonovitch[15] and also by Campbell and Green the latter at the UNSW in Australia. [16]

Given that CZ silicon samples as are conventionally used in silicon processing do not provide high gain photodetectors then the increased absorption of CZ silicon devices in the infrared, but without gain, is easily explained by texturing of the black silicon surfaces. The idea of laser texturing of silicon surfaces in photodetectors was reported by Russell et al. in 1992[17] and then again in detail in 2003 [18]. Yamamoto et al. have described in detail the experimental results of backside texturing of photodetectors [19] by laser ablation and we provided a simple analysis of their results by backside scattering of light in photodetectors [14]. The net result is that all of the claimed phenomena for black silicon, reduced reflectance, increased absorption in the infrared as claimed by Mazur, Carey and the SiOnyx et al. can be explained by old phenomena commonly know to those skilled in the art of silicon technology. One skilled in the art will however soon appreciate that laser ablation introduces a huge number of defects and that it virtually impossible to anneal all of these out. These defects are particularly detrimental to photodetectors and solar cells so “black silicon” as described by Mazur, Carey, and SiOnyx et al. is simply not likely to be useful or employed in such devices demonstrating any utility. Textured devices produced by chemical etch, however, are useful and are commonly used in solar cells being sold commercially in the USA since before 2009.[20]

Recently there have been attempts to apply black silicon as the front side texture in solar cells, the first of these by the National Renewable Energy Lab., NREL, [21] used a porous silicon etch on the front side to reduce reflectance. This works well in reducing the visible light reflectance of bare silicon wafers with absorption to a few per cent. It is not clear, however, if this provides any scattering of the light in the substrate. The texture comprises tall vertical structures, and 30% of the infrared light is still reflected with one side textured, the front side texture may be acting just as an antireflective layer with no scattering. A single polished silicon surface with no absorption in the substrate has a reflectance of 34% and a double side polished wafer with no absorption has a reflectance of 46%. In a collaborative project NREL and Natcore developed the blackest of all black silicon, also known as the “Blackest Solar Cell” that absorbs 99.7% sunlight . A metal catalyzes used as a porous silicon etch creates millions of holes on the surface of a silicon wafer already having a large texture. Natcore provided the liquid phase deposited oxide to fill the holes for passivation of the surface. [22] Even more recently SiOnyx used laser ablation [23] to create a fine texture on the front side of solar cells that already had an ISO texture (isotropic – acidic textured) wafers [24] but this made at best only a 0.3% improvement in conversion efficiency.

Texturing by chemical etch has also been previously disclosed for use in CMOS imagers. [25] However, the high density of defects introduced into the thin photodiodes by laser ablation [5] will result in a reduction in yield and increase in dark current and a consequent loss of utility .

Patents are supposed to benefit the public. The Constitution implicitly expresses this intent, the US Patent Office acknowledges this, and the Supreme Court has so interpreted it. Yet the current patent system fails miserably short of realizing this purpose. One example of the system's failure is the absence of a timely, inexpensive mechanism for invalidating the high number of bad patents being issued. As a result of this void, the public is suffering, and enormous wastes of expenditures of investor and public funding are incurred. There is as demonstrated by the previous example of "black silicon" a dire need for reform. The recent change by the America Invents Act in allowing an easier mechanism for third party submissions during patent prosecution [26] is a first step in this direction.

---

* Leonard Forbes is a semi-retired Professor and is currently America's most prolific living inventor in electrical sciences and technology.

References

[1] L. Forbes, "Unpublished Ph.D. Dissertation Work", University of Illinois, 1970.

[2] H. Jansen, M. de Boer, R. Legtenberg, and M. Elwenspoek, "The black silicon method: a universal method for determining the parameter setting of a fluorine-based reactive ion etcher in deep silicon trench etching with profile control," Journal of Micromechanics and Microengineering , Vol. 5, No. 2, 1995, p. 115.

[3] M. Hidaka, "Etching method(to avoid forming black silicon)," US Patent Application, No. 20070167011, 2007, pp. 1-17.

[4] Z. Huang, J.E. Carey, M. Liu, X. Guo, J. C. Campbell and E. Mazur, "Microstructured silicon photodetector," Appl. Phys. Letters, Vol. 89, No. 033506, 2006, pp. 1-3.

[5] J.E. Carey, X. Li, and N. J. McCaffrey Mar. 4, 2010   "High Sensitivity Photodetectors, Imaging arrays, and High Efficiency Photovoltaic Devices produced using Ion Implantation and Femtosecond Laser Irradiation," US Patent Application Publication, No. 20100052088, 2010, pp. 1-22, and also E. Mazur and J.E.Carey, "Silicon-based visible and near-infrared optoelectric devices," United States Patent, No. 7,781,856, 2010, pp. 1-30.

[6] S. M. Sze, "Physics of Semiconductor Devices." Wiley Interscience, New York, 2nd Ed., 1981, p. 746.

[7] C-T. Sah, L. Forbes and W.W. Chan, "A New Model of Negative Photocurrent," Science Bulletin of National Chiao-Tung University, Vol. V, No. 2, 1972, pp. 1-10.

[8] S. A. Boden and D. M. Bagnall, "Nanostructured Biomimetic Moth-eye Arrays in Silicon by Nanoimprint Lithography," Proc. of SPIE, Vol. 7401, No. 74010J, 2009 , pp. 1-12.

[9] The Times, London, UK, May 31, 2010 , Home Staff, "Bank Note Nanotechnology based on Butterfly Wings could beat Forgers." The Times, UK News, London, 2010 , pp. 1-2. http://www.thetimes.co.uk/tto/news/uk/article2534152.ece

[10] Von D. A. G. Bruggemann , "Berechnung Verschiedcner Physikalischer Konstanten von Heterogenen Substanzen," Annalen der Physik, 5. Folge, Band 24, 1935, pp. 636-664.

[11] R. A. Arndt, J. F. Allison, J. G. Haynos, and A. Meulenberg, Jr., "Optical properties of the COMSAT non-reflective cell," Proc. 11th IEEE Photovoltaic Spec. Conf., Scottsdale, Ariz., 6-8 May 1975, pp. 40-43.

[12] A.E. St John, "Multiple Internal Reflection Structure in a Silicon (Photo)Detector which is Obtained by Sandblasting," US Patent, No. 3,487,223, 1969, pp. 1-3.

[13]   W. Czubatyj, R. Singh, J. Doehler, D.D. Allred, and J.M. Reyes   "Photovoltaic Device having Incident Radiation Directing means for Total Internal Reflection," US Patent, No. 4,419,533, 1983, pp. 1-18.

[14] L. Forbes, "Texturing, reflectivity, diffuse scattering and light trapping in silicon solar cells," Solar Energy, Vol. 86, No. 1, 2012, pp. 319-325.

[15] E. Yablonovich, and G.D. Cody, "Intensity Enhancement in Textured Optical Sheets for Solar Cells," IEEE Trans. on Electron Devices, Vol. ED-29, 1982. pp. 300-305.

[16] P. Campbell and M. A. Green, "High performance light trapping textures for monocrystalline silicon solar cells," Solar Energy Materials & Solar Cells. Vol. 65, 2001, pp. 369-375.

[17] United States Patent 5,164,324 S.D. Russell, D. A. Sexton and E.P. Kelley, "Laser Texturing, " US Patent, No. 5,164,324, 1972, pp. 1-12.

[18] S. D. Russell, A. D. Ramirez, and E. P. Kelley, "Nanosecond Excimer Laser Processing for Novel Microelectronic Fabrication," SSC Pacific Technical Reports , Vol. 4, Navigation and Applied Sciences, 2003, pp. 228-233.
http://www.spawar.navy.mil/sti/publications/pubs/td/3155/5a_S4papers/NanoXLaser.pdf

[19] K. Yamamoto, A. Sakamoto, T. Nagano, and K. Fukumitsu, "NIR sensitivity enhancement by laser treatment for Si detectors," Nuclear Instr. and Meth. Phys., Vol. A624, 2010, pp. 520-523.

[20] Z. Shi, S. Wenham, J. Ji, S. Partlin, and A. Sugianto, "Mass Production of the Innovative Pluto Solar Cell Technology," SunTech, White paper , 2011. http://am.suntech-power.com/

[21] H.-C. Yuan, V. E. Yost, M. R. Page, P. Stradins, D. L. Meier and H. M. Branz, "Efficient black silicon solar cell with a density-graded nanoporous surface: Optical properties, performance limitations, and design rules," Appl. Phys. Lett., Vol. 95, No. 123501, 2009, pp. 1-3.

[22] Maria Faur, Mircea Faur, D. Flood, S.G. Bailey and Horia M. Faur, "Room temperature wet chemical growth process of SiO based oxides on silicon," US Patent, No. 6,080,683, 2007, pp. 1-24.

[23] C. Vineis, M. Levy-Finklshtein, J. Carey, G. Knight, E. Wefringhaus and R. Harney, "Ultrafast Laser Texturing for Enhanced Solar Cell Performance and Lower Cost," 2012.
http://www. sionyx.com/pdf/solarcellperformancewhitepaper.pdf

[24] T. Geipel, S. Pingel, J. Dittrich, Y. Zemen, G. Kropke, M. Wittner, and J. Berghold, "Comparison of acidic and alkaline textured multicrystalline solar cells in a solar panel production," 2010.
http://www.solon.com/export/sites/default/solonse.com/_downloads/global/article-pid/Geipel_et_al_texturization.pdf

[25] D. Wells and S. P. Leiphart, "Light sensor having undulating features for CMOS imager," US Patent, No. 7,456,452, 2008, pp. 1-19.

[26] US Patent Office, "Preissuance Submissions by Third Parties Final Rules," 2012.
http://www.gpo.gov/fdsys/pkg/FR-2012-07-17/pdf/2012-16710.pdf