Solution-processed photodetectors from colloidal silicon nano/micro particle composite

Chang-Ching Tu,[1,2,*] Liang Tang,[2] Jiangdong Huang,[2] Apostolos Voutsas,[2] and Lih Y. Lin[1]

[1]*Department of Electrical Engineering, University of Washington, Seattle, WA, 98195, USA*
[2]*Materials and Device Applications Laboratory, Sharp Laboratories of America, Inc., Camas, WA98607, USA*
**tucc@u.washington.edu*

Abstract: We demonstrate solution-processed photodetectors composed of heavy-metal-free Si nano/micro particle composite. The colloidal Si particles are synthesized by electrochemical etching of Si wafers, followed by ultra-sonication to pulverize the porous surface. With alkyl ligand surface passivation through hydrosilylation reaction, the particles can form a stable colloidal suspension which exhibits bright photoluminescence under ultraviolet excitation and a broadband extinction spectrum due to enhanced scattering from the micro-size particles. The efficiency of the thin film photodetectors has been substantially improved by preventing oxidation of the particles during the etching process.

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References and links

1. I. Gur, N. A. Fromer, M. L. Geier, and A. P. Alivisatos, "Air-stable all-inorganic nanocrystal solar cells processed from solution," Science **310**(5747), 462–465 (2005).
2. J. M. Luther, M. Law, M. C. Beard, Q. Song, M. O. Reese, R. J. Ellingson, and A. J. Nozik, "Schottky solar cells based on colloidal nanocrystal films," Nano Lett. **8**(10), 3488–3492 (2008).
3. E. H. Sargent, "Infrared photovoltaics made by solution processing," Nat. Photonics **3**(6), 325–331 (2009).
4. D. C. Oertel, M. G. Bawendi, A. C. Arango, and V. Bulovic, "Photodetectors based on treated CdSe quantum-dot films," Appl. Phys. Lett. **87**(21), 213505 (2005).
5. G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levina, and E. H. Sargent, "Ultrasensitive solution-cast quantum dot photodetectors," Nature **442**(7099), 180–183 (2006).
6. J. P. Clifford, G. Konstantatos, K. W. Johnston, S. Hoogland, L. Levina, and E. H. Sargent, "Fast, sensitive and spectrally tuneable colloidal-quantum-dot photodetectors," Nat. Nanotechnol. **4**(1), 40–44 (2009).
7. V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, "light-emitting diodes made from cadmium selenide nanocrystals and a semiconductor polymer," Nature **370**(6488), 354–357 (1994).
8. J. Zhao, J. A. Bardecker, A. M. Munro, M. S. Liu, Y.-H. Niu, I.-K. Ding, J. Luo, B. Chen, A. K.-Y. Jen, and D. S. Ginger, "Efficient CdSe/CdS quantum dot light-emitting diodes using a thermally polymerized hole transport layer," Nano Lett. **6**(3), 463–467 (2006).
9. A. M. Derfus, W. C. W. Chan, and S. N. Bhatia, "Probing the cytotoxicity of semiconductor quantum dots," Nano Lett. **4**(1), 11–18 (2004).
10. Z. Ding, B. M. Quinn, S. K. Haram, L. E. Pell, B. A. Korgel, and A. J. Bard, "Electrochemistry and electrogenerated chemiluminescence from silicon nanocrystal quantum dots," Science **296**(5571), 1293–1297 (2002).
11. J. G. C. Veinot, "Synthesis, surface functionalization, and properties of freestanding silicon nanocrystals," Chem. Commun. (Camb.) (40): 4160–4168 (2006).
12. X. Zhang, D. Neiner, S. Wang, A. Y. Louie, and S. M. Kauzlarich, "A new solution route to hydrogen-terminated silicon nanoparticles: synthesis, functionalization and water stability," Nanotechnology **18**(9), 095601 (2007).
13. J. D. Holmes, K. J. Ziegler, R. C. Doty, L. E. Pell, K. P. Johnston, and B. A. Korgel, "Highly luminescent silicon nanocrystals with discrete optical transitions," J. Am. Chem. Soc. **123**(16), 3743–3748 (2001).
14. X. Li, Y. He, S. S. Talukdar, and M. T. Swihart, "Process for preparing macroscopic quantities of brightly photoluminescent silicon nanoparticles with emission spanning the visible spectrum," Langmuir **19**(20), 8490–8496 (2003).
15. L. Mangolini, E. Thimsen, and U. Kortshagen, "High-yield plasma synthesis of luminescent silicon nanocrystals," Nano Lett. **5**(4), 655–659 (2005).
16. S.-M. Liu, S. Sato, and K. Kimura, "Synthesis of luminescent silicon nanopowders redispersible to various solvents," Langmuir **21**(14), 6324–6329 (2005).

17. Z. Yamani, W. H. Thompson, L. AbuHassan, and M. H. Nayfeh, "Ideal anodization of silicon," Appl. Phys. Lett. **70**(25), 3404 (1997).
18. G. Belomoin, J. Therrien, and M. Nayfeh, "Oxide and hydrogen capped ultrasmall blue luminescent Si nanoparticles," Appl. Phys. Lett. **77**(6), 779 (2000).
19. Z. Kang, C. H. A. Tsang, Z. Zhang, M. Zhang, N. B. Wong, J. A. Zapien, Y. Shan, and S.-T. Lee, "A polyoxometalate-assisted electrochemical method for silicon nanostructures preparation: from quantum dots to nanowires," J. Am. Chem. Soc. **129**(17), 5326–5327 (2007).
20. E. D. Palik, "Handbook of optical constants of solids," Elsevier (1998).
21. M. H. Nayfeh, S. Rao, O. M. Nayfeh, A. Smith, and J. Therrien, "UV photodetectors with thin-film Si nanoparticle active medium," IEEE Trans. NanoTechnol. **4**(6), 660–668 (2005).

1. Introduction

Colloidal inorganic semiconductor nanocrystals share the important advantages of organic materials such as low-temperature solution-processing and controllable synthesis. Meanwhile, compared to organics, nanocrystals-based devices with proper particle surface passivation exhibit broader absorption spectrum and more efficient charge transport. Optoelectronic applications based on these nanomaterials include solar cells [1–3], photodetectors [4–6] and light-emitting diodes (LEDs) [7,8]. However, these compound semiconductor nanocrystals, usually Pb- or Cd-chalcogenide based, are found to be toxic due to the heavy metal ingredients [9] which curtail their potential for large-scale production and commercialization.

Unlike compound semiconductors, silicon is biocompatible and electrochemically stable [10]. Furthermore, owing to the needs of the microelectronics industry, Si has been well studied for the past several decades. Therefore, the development of solution-processable colloidal Si materials which retain some bulk crystalline characteristics while achieving enhanced optical properties due to high degree of confinement implies an interesting path of research. Extensive works have been contributed to the synthesis of Si nanoparticles, including solution-based precursor reduction [11, 12] or thermal decomposition [13], laser induced silane aerosol pyrolysis [14], nonthermal plasma synthesis [15] and etching of silicon rich oxide (SRO) thin film [16]. However, these methods invariably require critical processing condition, special equipment and complex purification procedures. On the other hand, it has been reported that electrochemical etching which only requires commercially available Si wafers, common electrolyte and is performed in an ambient condition can be utilized to synthesize photoluminescent porous Si nanostructures [17]. Free standing Si nanoparticles are then prepared by pulverizing the porous Si wafers in an ultra-sonication bath [18,19]. This method is especially promising for low-cost, large-quantity and high-throughput production of Si nanoparticles. Notably, by varying etching condition, not only nanoparticles but also micro-scale wires or pillars can be generated [19].

Here we demonstrate thin film photodetectors fabricated from colloidal Si nano/micro particle composite. A method of surface passivation by alkyl ligands is developed, so that the particles can form a stable colloidal suspension. By solution-processing methods such as spin-coating or drop-casting, uniform depositions can be achieved in a room condition and on a variety of substrates. The resulting thin films were measured in ambient atmosphere and no significant degradation of the photoconductivity property was observed. In terms of device structure, inclusion of micro-structures in addition to nanoparticles in the thin films shows beneficial effects in both device fabrication and performance for light-absorbing applications, such as photodetectors and solar cells. It is easier to use micro-size particles to deposit thicker films which are especially desirable for indirect band gap semiconductors like Si to achieve high absorption. The presence of these micro-size particles increases scattering within the film and therefore overall efficiency. Furthermore, micro-particles with a smaller surface-to-volume ratio than nanoparticles suffer less from the effect of surface ligand passivation which increases inter-particle spacing and decreases charge carrier mobility in the thin film.

2. Fabrication

We electrochemically etched p-type boron-doped Si wafers with (100) orientation and 5 – 20 ohm-cm resistivity in a mixture of HF, methanol, H_2O_2 and polyoxometalates (POMs), where the latter two function as catalyst [17–19]. At high current density (>10 mA / cm^2) and

etching time of several hours, typical etched surface structures are micro-pores of diameter around 2 μm, as shown in Fig. 1(a), while at low current density (<10 mA / cm^2) and short etching time, nano-scale porous surface is found, as shown in Fig. 1(b). Generally, more micro-structures are found close to the meniscus region (air-liquid interface), as a result of gradually decreasing current density away from the liquid surface. After electrochemical etching, the Si wafer surface exhibited redish / orangish photoluminescence under 365 nm ultraviolet (UV) lamp illumination, as shown in Fig. 1(f). With proper etching conditions, electrochemically etched Si surface should be mostly hydrogen-terminated, as suggested by Fourier-transform infrared (FTIR) spectroscopy data in literature [17, 19], and become hydrophobic. For more saturated hydrogen-passivation and removal of carbon and oxide residues, the etched Si wafer was treated in diluted HF prior to further steps.
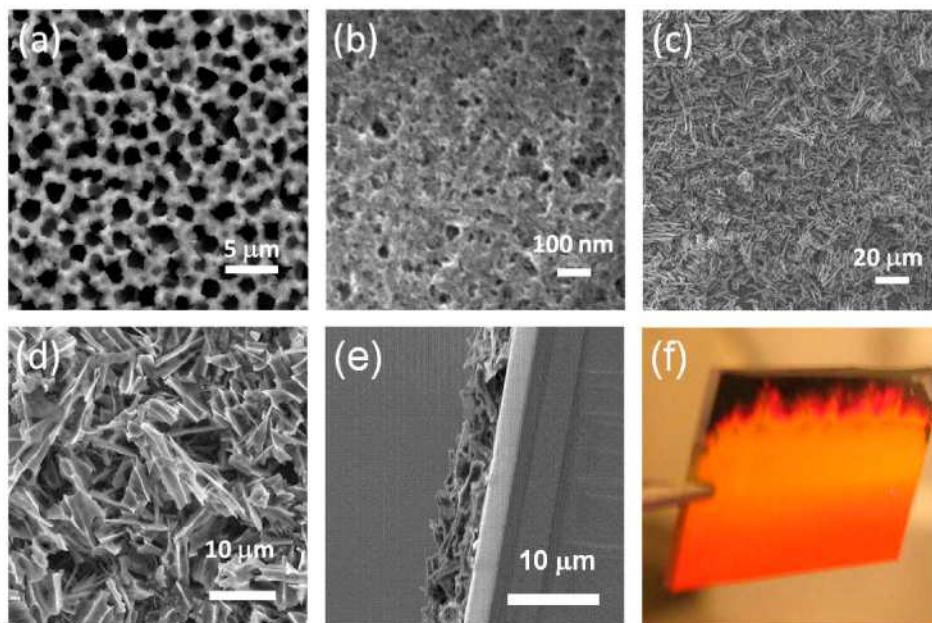

Fig. 1. The SEM images of Si wafer surface after being electrochemically etched at (a) high and (b) low current density. The SEM images of the drop-casted Si nano/micro particle composite thin film in (c) lower magnification, (d) higher magnification and in (e) cross-sectional view. (f) The redish / orangish photoluminescence of the silicon wafer under 365 nm UV lamp illumination after electrochemical etching and before ultra-sonication.

Hydrogen-terminated surface can be converted to alkyl-termination to achieve a stable surface passivation. The unsaturated double bond of 1-octene is reacted with the hydride termination on Si surface through hydrosilylation reaction with chloroplatinic acid as catalyst, resulting in octane-modified Si surface [12]. After the surface modification, the porous Si wafer immersed in 1-octene / hexane (1 / 1) as dispersion medium is ultra-sonicated for 5 minutes. Experimentally, we found that without hydrosilylation reaction, the Si nano/micro particle composites could suspend for only a few minutes after ultra-sonication and then began to agglomerate into millimeter-size precipitates; whereas, the octane-modified composites kept suspension for several days without obvious aggregation.

The thin film is formed by drop-casting the colloidal Si suspension over the electrodes where *I-V* characteristics of the photodetectors are measured. To increase the coverage of Si nano/micro particles, multiple-layers deposition and condensation of the colloidal suspension are employed. Here approximately 6 cm2 of etched Si wafer surface was ultra-sonicated in 1 mL of the 1-octene / hexane solvent. Typical SEM images of the thin film after 40 layers of deposition are shown in Fig. 1(c) and (d), where most of the drop-casted region is covered with rod shape (~10 μm in length and ~2 μm in diameter) micro-particles while few exposed

regions can still be observed. The average thickness of the thin film is around 4 μm, as shown in the cross-sectional SEM image in Fig. 1(e). The fill-factor of the thin film is estimated to be around 34%. Having a stable colloidal suspension and using highly evaporative solvent as dispersion medium are essential for fabricating uniform thin films. To further increase the film uniformity, more condensation of the suspension is needed so that fewer drop-casting depositions are required to achieve high coverage. Inkjet printing of the colloidal Si material is a promising alternative method to fabricate large area and uniform thin films. To improve the charge carrier transport property, passivating the particle surface with shorter ligands or imbedding the particles in conductive polymers is under research.
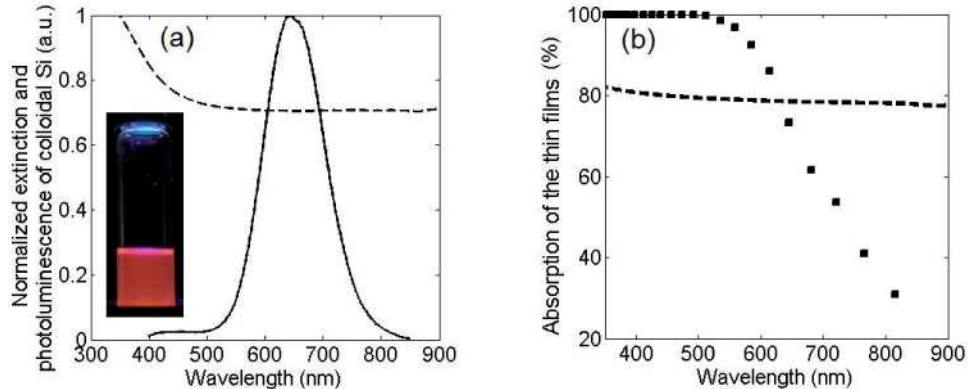

Fig. 2. (a) The normalized extinction (dashed) and photoluminescence (solid) spectra of the colloidal Si nano/micro particle suspension measured in 1-octene. The inset photograph shows the redish / orangish photoluminescence of the colloidal suspension under 365 nm UV excitation. (b) The absorption spectra of the 40-layer Si nano/micro particle composite thin film (dashed) and a 4 μm-thick Si single crystalline thin film (square).

3. Experiment and discussion

The extinction (absorption + scattering) and photoluminescence spectra of the colloidal Si nano/micro particle composite measured in solution are shown in Fig. 2(a). The absorption spectrum of the composite thin film with 40 layers of deposition is shown in Fig. 2(b), while the absorption spectrum of a 4 μm-thick Si single crystalline thin film is plotted for comparison [20]. Due to enhanced scattering from the micro-size particles, both extinction of the colloidal suspension and absorption of the composite thin film show relatively flat spectra from visible to near-infrared (near-IR). Besides, the reflectance of the composite thin film was measured to be less than 2% from UV to IR, suggesting high surface roughness due to micro-size particles. Notably, in Fig. 2(b), the Si single crystalline thin film has more absorption than the composite thin film for wavelength below ~650 nm because the crystalline thin film has no void structure as the Si nano/micro composite which has fill-factor around 34%. However, in the IR wavelengths, the light trapping micro-structures in the composite thin film greatly enhances the absorption. This can be of potential interest for photovoltaic researchers to harvest solar energy in the infrared regime. In Fig. 2(a), under the illumination of 365 nm UV light, the Si nano/micro composite exhibits photoluminescence with a peak wavelength at 633 nm and full-width-at-half-maximum (FWHM) of 121 nm. The inset photograph shows the redish / orangish photoluminescence of the suspension.

For photo-response measurement, we use a 405 nm laser with intensity 45.9 mW / cm^2 as the light source. The devices use lateral comb-shape electrodes of 10 μm gap and made of 150 nm Au thin film on a silicon dioxide substrate as shown in the inset of Fig. 3(a). The active area which is defined as the area between the comb fingers is 6.81×10^{-4} cm^2, although the Si particles do not completely cover all the area. Figure 3(a) shows the *I-V* measurement results in dark and under 405 nm laser illumination, and Fig. 3(b) shows the responsivity and external quantum efficiency (EQE) of the photodetectors versus applied voltages. At applied

voltage = 48 V, the photodetector shows a photocurrent = 1.62 µA, which corresponds to responsivity = 51.8 mA / W and EQE = 15.9%. The Si composite thin film between the Au electrodes serves as a photoconductor which shows photoconductivity upon illumination. Experimentally, we found that the efficiency was greatly influenced by oxide residues which are formed during the electrochemical etching process. The electrolyte, mostly methanol, gradually evaporates during the etching process. The lowered meniscus level leaves some etched Si wafer surface which is still wetted with residual H_2O_2 exposed in the air and thus oxidized. The photodetector made from these Si nano/micro particles with more oxidation showed significantly lower EQE (~1%, also plotted in Fig. 3(b)) likely due to the increased concentration of recombination centers which decreases charge carrier extraction efficiency. To solve this problem, a constant meniscus level was maintained by frequently refilling the electrolyte or slowly moving the Si wafer into the meniscus accordingly. The dark current *I-V* curve in Fig. 3(a) shows higher slope at higher bias voltages, indicating that the charge carrier transport in the thin film is field-assisted likely due to the presence of octane ligands as barriers. To further increase the photodetector efficiency, annealing or sintering processes that can appropriately remove these organic layers are being investigated.
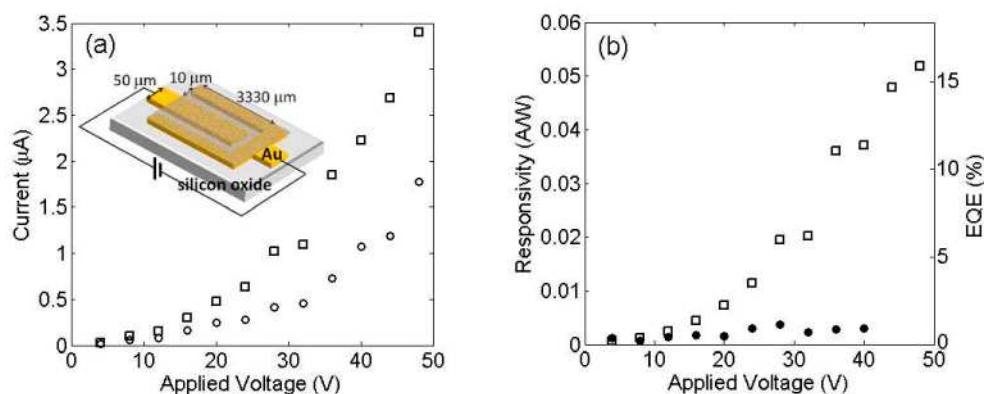

Fig. 3. (a) The *I-V* measurement results of the photodetector in dark (circle) and under 405 nm laser illumination (square). The inset illustrates the structure of the comb-shape lateral electrodes used for photodetection measurement. The shaded area illustrates the region covered with Si nano/micro particle composite. (b) The responsivity and external quantum efficiency (EQE) vs. applied voltages of the photodetectors composed of nano/micro particles with less (square) and more (dot) oxidation during the etching process.

In literature, Si nanoparticles based UV photodetectors were fabricated by "electrochemical-plating" Si nanoparticles (1 nm in diameter) on p-type Si substrates and exhibited responsivity of 350-750 mA / W under 365 nm mercury lamp excitation [21]. Such high sensitivity is attributed to the uniform particle size distribution which enables resonant tunneling [21]. Compared to the electrochemical-plating technique, the solution-based fabrication method used in this work is potentially lower-cost and shows more flexibility in substrate selection. Besides, since the micro-size particles have sizes much larger than the Si Bohr exciton radius (4.9 nm), there is no quantum confinement effect and the energy band gap is the same as crystalline Si. As a result, our composite thin film has additional photodetection capability in the visible wavelengths. A photodetector fabricated by the same process except a slightly different etching condition has demonstrated EQE = ~14% under 650 nm laser excitation.

4. Conclusion

In summary, we have fabricated thin film photodetectors consisting of heavy-metal-free colloidal Si nano/micro particle composite, as compared to toxic Pb- or Cd-chalcogenide based nanocrystals, by a solution-processing method. The colloidal Si particles were synthesized by electrochemical etching method. Due to the octane-modified surface

passivation, the particles form a stable suspension with broadband extinction spectrum attributed to the enhanced scattering from the micro-size particles and bright redish / orangish photoluminescence under UV excitation. By avoiding oxidation during the etching process, the photodetectors showed a more than 10-fold increase in efficiency likely due to decreased concentration of surface recombination centers in the thin film. The colloidal Si material presented here can be potentially applied for other optoelectronic or electronic devices, such as solar cells, LEDs and thin-film transistors (TFTs), and be fabricated on flexible plastic substrates by solution-processing methods.

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