Absorptivity enhancement of black silicon using electroless Cu plating

Ahmed Khaled[a], Magdy Hussein[a,b], Ahmed A. Elsayed[a.d], Frédéric Marty[d], Elyes Nefzaoui[d], Tarik Bourouina[d],Yasser M. Sabry[a,c] and Diaa Khalil[a,c]

[a]Faculty of Engineering, Ain-Shams University, 1 Elsarayat St. Abbassia, Cairo, Egypt; [b]National Institute of Laser Enhanced Sciences Engineering Department, Cairo University, Cairo, Egypt; [c]Si-Ware Systems, 3 Khalid Ibn Al-Waleed St., Heliopolis, Cairo, Egypt; [d]Université Paris-Est, Laboratoire ESYCOM, ESIEE Paris, F-93162 Noisy-le-Grand Cedex,Paris, France

ABSTRACT

Black silicon (BSi) are silicon substrates that have a needle-like morphological surface in the nano/micro scale. These nano/micro structures suppress the reflection of light off the BSi surface and traps the light, enabling a variety of applications such as high efficiency solar cells, photodetectors and as recently reported infrared (IR) radiation sources. The BSi can be fabricated using various methods such as femto-second laser treatment, chemical etching and cryogenic deep reactive ion etching (DRIE). In this work, lightly-doped BSi is fabricated using cryogenic DRIE in a maskless manner and its transmittance and reflectance are measured using an integrating sphere and a spectrometer in the NIR wavelength range of 1300 nm - 2500 nm. Then, the surface is cleaned and copper (Cu) is deposited on the BSi using the wet deposition technique of electroless plating, enabling high throughput coating. The copper ions are deposited on the BSi surface in a Cu sulphate solution, taking advantage of the conformity of the plating to the nano/micro structures of the BSi targeting lower reflectance and higher absorptivity. The Cu-plated BSi is measured and observed to have a minimum reflectance of 10% compared to 30% in the case of BSi, and a minimum transmittance of 10% compared to 40% in the bare black silicon. Thus, the Cu-plated BSi has a maximum absorptivity of about 80% compared to 30% in the bare BSi. The absorptivity is found to decrease with increasing the wavelength. This enhancement using the electroless Cu plating further qualifies the BSi as a candidate for NIR thermal light sources.

Keywords : Black silicon (BSi), Electroless plating, Metalized black silicon, Light sources, Absorbers.

1. INTRODUCTION

Polished silicon substrates have high reflectivity which disqualifies it from being used in applications that require high absorptivity materials such as photodetectors, solar cells and black body radiation sources. One of the techniques used to reduce the reflectivity of silicon substrates, thus increasing its absorptivity, is the nano/micro-structuring of the silicon surface to produce what is known as Black Silicon[1,2]. The produced black silicon surface has a needle-like morphological surface. The incident optical radiation on the black silicon experiences multiple reflections between the nano/micro needles on its surface. This reduces the overall reflection coefficient of the black silicon substrate causing it to appear black in the visible range and hence the name black silicon. Consequently, the black silicon opens the door for many applications such as high efficiency solar cells[3–5], photodetectors[6] and as recently reported infrared (IR) radiation sources[7,8]. However, the reflection coefficient could be further reduced if the needle like structures on the surface of the black silicon were confromally plated by a metal. This idea is close to the principle of operation of the microwave anechoic chambers where metal cones are used to suppress the microwaves reflection off the walls of the chamber enabling accurate measurements of microwave devices. The metal used in this paper is copper. An interesting metal plating technique is the electroless plating[9,10] which has many applications such as coating of on-chip radio frequency inductors[11] and low resistivity metal contacts of solar cells[12,13]. This technique is used in this paper to provide conformal metal layer on the needle-like structures on the black silicon surface without destroying them. The absorptivity enhancement provided by the copper plating of the black silicon further qualifies the black silicon as a candidate for integrated NIR thermal light sources. The fabrication of the needle-like nano/micro structure on the silicon surface is discussed in section 2. In section 3, the electroless plating of copper on the black silicon is discussed and the used recipe is given. Finally, in section 4, the experimental setups used to measure the absorptivity of the copper plated black silicon are shown and the results are discussed.

2. BLACK SILICON FABRICATION

Black silicon can be fabricated in many ways such as femto-second laser treatment, chemical etching and cryogenic deep reactive ion etching[14]. In this paper, lightly-doped black silicon is fabricated using a mask-free cryogenic deep reactive ion etching process. The fabrication was done with the same process as in a previous work[1]. The plasma of Sulphur Hexafluoride (SF_6) and Oxygen (O_2) were used to fabricate the black silicon. The Sulphur Hexafluoride gas acts as a source of fluorinated radicals (F*) which react with silicon as follows :

$$Si + 4F^* \rightarrow SiF_4$$

The formed SiF_4 is volatile. Simultaneously, the fluorinated radicals react with the silicon and the oxygen radicals as follows :

$$Si + 4F^* \rightarrow SiF_4$$

$$SiF_x + yO^* \rightarrow SiO_yF_x$$

The formed SiO_yF_x is formed on the side walls of the etched silicon and acts as a passivation layer which stops the side wall etching enabling the formation of the needle-like nano/micro-structures of the black silicon. It is to be noted that this passivation layer is volatile at room temperature, so this process is carried out at cryogenic temperature. The used process parameters are summarized in Table 1.

Process parameter	**Value**
Name of the reactor used	Alcatel 601E
Power of the reactor	1000 W
Gas pressure	1.5 Pa
Oxygen gas flow rate	10 sccm
Sulphur Hexafluoride gas flow rate	200 sccm
Wafer type	single-crystalline n-type silicon (100) wafer

Wafer thickness	525 um
Wafer resistivity	1-20 Ω.cm

Table 1. Black silicon fabrication process parameters

An SEM of the fabricated black silicon is shown in Fig.1. The height of the needle-like nano/micro-structures on the black silicon surface is 1-3 µm and has a periodicity of 0.5-1 µm.

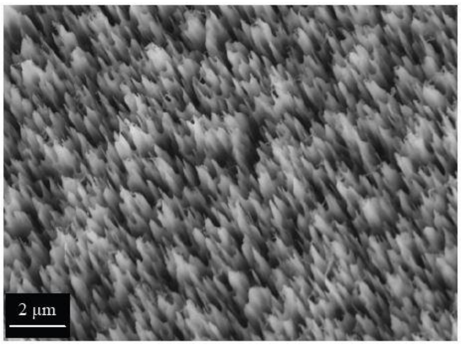

Figure 1. An SEM of the surface of the fabricated black silicon

3. ELECTROLESS PLATING OF COPPER ON BLACK SILICON

Electroless plating has many advantages over electroplating and sputtering. In the electroless plating technique, the metal is deposited on the surface of the substrate from a chemical solution so, it doesn't require a lot of equipments which makes the electroless plating a low cost solution and that was one of the main drivers of using it in the contacts of the solar cells instead of the formerly used silver paste[13]. Another advantage of the electroless plating and the one we care about most in this paper is the conformal plating of the substrate. This allows the conformal plating of the needle-like structures on the surface of the black silicon thus preserving the structure shape and its beneficial properties of trapping the input optical radiation. If sputtering had been used, these needle-like structures would have been destroyed and the property of trapping of the input optical radiation would have been lost. To plate the black silicon, first, the native oxide layer on the surface of the silicon is removed using Hydrogen Fluoride (HF)[15]. 2.5 mL of 40% Hydrogen Fluoride were mixed with 50 mL of distilled water and the samples were dipped in the mixture for a minute. The chemical reaction takes place as follows :

$$SiO_2 + 6HF \rightarrow 2H^+ + SiF_6^{2-} + 2H_2O$$

In electroplating, the metal ions found in the metal salt solution are attracted to the surface of the substrate due to the voltage applied to the substrate and the metal is reduced and deposited on the surface of the substrate[16]. However, in electroless plating, no voltage is applied to the substrate so another mechanism for metal deposition on the silicon surface is required. Mechanisms used to plate the black silicon with copper can be found in the literature[10,17]. To plate the black silicon samples, the samples are dipped in a mixture of two solutions and the thickness of the copper deposited on the silicon surface is controlled by the deposition time. The first solution is 2.5 mL of 40% Hydrogen Fluoride in 50 mL of distilled water and the second solution is 8 mg of copper sulphate ($CuSO_4$) in 50 mL of distilled water. The chemical reactions happening in this mechanism mimic the oxidation and reduction reactions that happen in the case of the electroplating. At first, the oxidation reaction takes place as follows :

$$Si + 6F^- \rightarrow SiF_6^{2-} + 4e^-$$

The resultant SiF_6^{2-} is soluble. Then, the reduction reaction takes place as follows :

$$2Cu^{2+} + 4e^- \rightarrow 2Cu$$

The overall reaction is as follows :

$$Si + 6F^- + 2Cu^{2+} \rightarrow SiF_6^{2-} + 2Cu$$

The resultant Cu is deposited on the surface of the black silicon. It is to be noted that the fact that n-type silicon is macroscopically neutral in charge but microscopically, the surface has roaming negative charges help attract the metal ions from the metal solution on to the surface of the silicon to be reduced. In this paper, three copper coated black silicon samples with three different thicknesses were fabricated by controlling the time of deposition. Their absorptivity have been measured and the results are discussed in the following section.

4. EXPERIMENTAL SETUP AND MEASUREMENTS

To measure the absorptivity of the black silicon samples, the reflection and the transmission of the samples are measured and the absorptivity is calculated as follows :

$$Absorptivity\ coefficient = 1 - reflection\ coefficient - transmission\ cofficient$$

4.1 Reflection measurement setup

The setup used to measure the reflection of the samples is shown in Fig.2. The setup is based on using an integrating sphere with a fourier transform infrared (FT-IR) spectrometer[18]. An NIR light source was used with a lens in a 2F configuration to focus the light on the black silicon samples where F is the focal length of the lens.

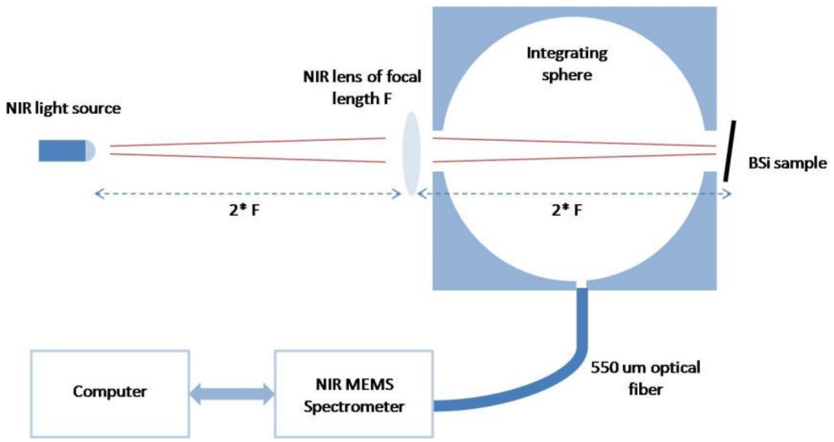

Figure 2. Reflection measurement setup

The samples are slightly titled (< 10^o) so that the reflected light hits the inside of the integrating sphere. The reflected light off the samples experience multiple reflection on the inside of the spheres till it is uniformly distributed. After that, the light is sampled through a 550 um fiber and observed by a fourier transform infrared spectrometer in the wavelength range of 1300-2500 nm. An uncoated black silicon sample measurement is recorded and divided by a background measurement when the sample is replaced by a spectralon to get the actual sample reflection spectrum shown in Fig.3.

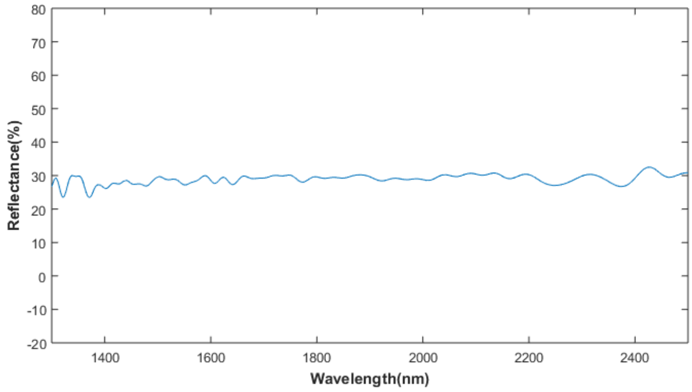

Figure 3. Bare BSi reflection measurement

After that, the copper coated black silicon samples were measured and the results are shown in Fig.4. It is noticed that reflection coefficient is considerably reduced to be 10-18 % instead of 30 % in the case of the uncoated samples. It is also noticed that the reflection is lower when the copper thickness is lower. This can be due to the fact that the copper starts filling the black silicon structure when the deposition time increases and the multiple reflection of incident optical radiation is reduced and hence the higher reflection coefficient.

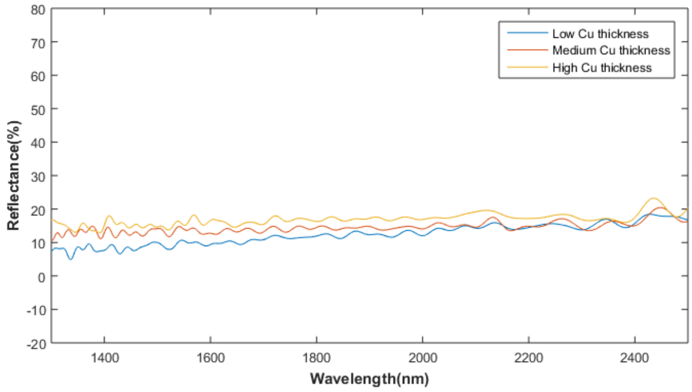

Figure 4. Cu coated BSi reflection measurement

4.2 Transmission measurement setup

The setup used to measure the reflection of the samples is shown in Fig.5. In this setup, the light output from the NIR source is collimated on the input port of the sphere. First, a background measurement is taken. After that, an uncoated black silicon sample was placed at the input port of the sphere closing it. The uncoated sample spectrum was obtained by dividing the sample measurement over the background one. The result is in Fig.6.

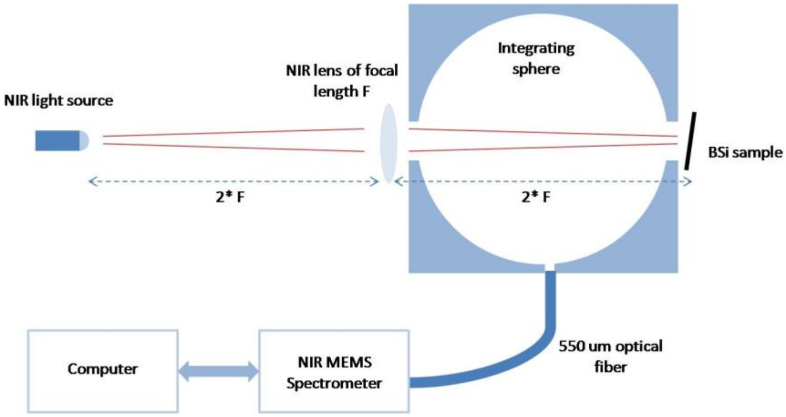

Figure 5. Transmission measurement setup

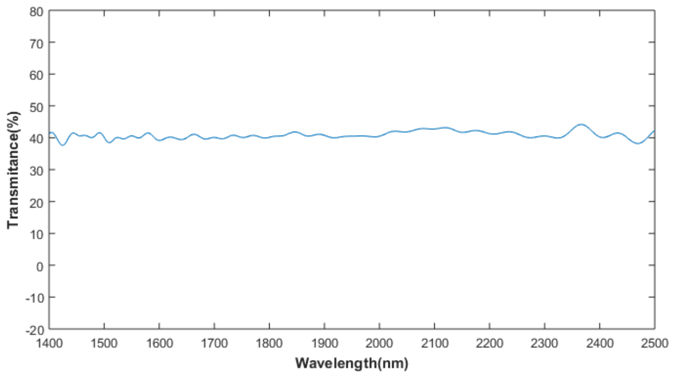

Figure 6. Bare BSi transmission measurement

After that, the copper coated black silicon samples were measured and the results are shown in Fig.7. It is noticed that transmission coefficient is considerably reduced to be 10-30 % instead of 40 % in the case of the uncoated samples. It is also noticed that the transmission is lower when the copper thickness is higher. This is due to the fact that the incident optical radiation experiences more attenuation as it propagates through higher thicknesses of copper.

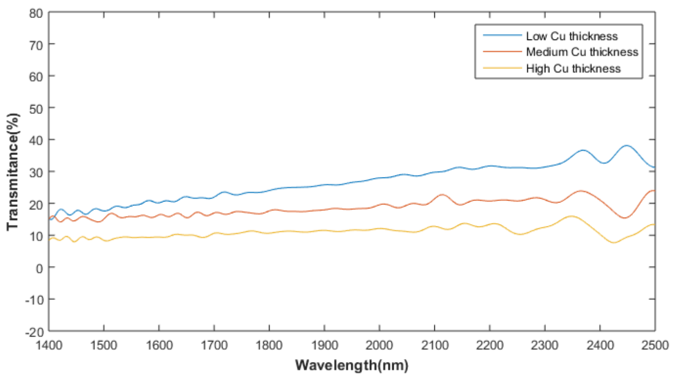

Figure 7. Cu coated BSi reflection measurement

4.3 Absorptivity calculation

Based on the transmission and reflection measurements of the samples, he absorptivity was calculated and the result is shown in Fig.8. It is noticed that the transmission coefficient trend takes over and the absorptivity coefficient decreases as the copper thickness increases. It is noticed that absorptivity coefficient is considerably enhanced to be 50-80 % instead of 30 % in the case of the uncoated samples. This considerable enhancement in the absorptivity further qualifies the copper coated black silicon as a strong candidate material for efficient photodetectors, solar cells and integrated black body radiation sources that can be used with MEMS spectrometers for gas sensing applications[19,20].

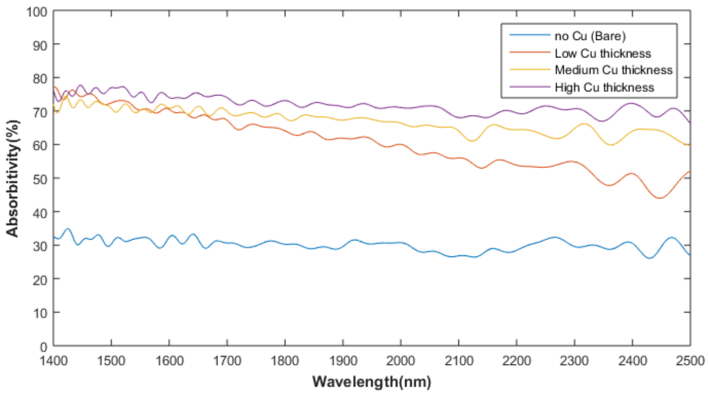

Figure 8. Absorptivity of bare and Cu coated BSi

5. CONCLUSION

In this work,lightly-doped BSi is fabricated using cryogenic DRIE in a maskless manner and electroless plated using Cu. The transmittance and reflectance are measured using an integrating sphere and a spectrometer in the NIR wavelength range of 1300 nm - 2500 nm. The Cu-plated BSi has a minimum reflectance of 10 % compared to 30 % in the case of BSi, and a minimum transmittance of 10 % compared to 40 %, respectively. Thus, the Cu-plated BSi has a maximum absorptivity of about 80% compared to 30% in the BSi. The absorptivity is found to decrease with increasing the wavelength.

REFERENCES

[1] Elsayed, A. A., Sabry, Y. M., Khalil, D., Marty, F. and Bourouina, T., "Optical diffuse reflectance of Black Silicon and its isotropicity," 2016 URSI Asia-Pacific Radio Sci. Conf. URSI AP-RASC 2016(August) (2016).

[2] Elsayed, A. A., Sabry, Y. M., Marty, F., Bourouina, T. and Khalil, D., "Optical modeling of black silicon using an effective medium/multi-layer approach," Opt. Express **26**(10), 13443 (2018).

[3] Yoo, J., Yu, G. and Yi, J., "Black surface structures for crystalline silicon solar cells," Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. **159**–**160**(C), 333–337 (2009).

[4] Oh, J., Yuan, H. C. and Branz, H. M., "An 18.2%-efficient black-silicon solar cell achieved through control of carrier recombination in nanostructures," Nat. Nanotechnol. **7**(11), 743–748 (2012).

[5] Yao, Y., Rodriguez, J., Cui, J., Lennon, A. and Wenham, S., "Uniform plating of thin nickel layers for silicon solar cells," Energy Procedia **38**, 807–815 (2013).

[6] Su, Y., Li, S., Wu, Z., Yang, Y., Jiang, Y., Jiang, J., Xiao, Z., Zhang, P. and Zhang, T., "High responsivity MSM black silicon photodetector," Mater. Sci. Semicond. Process. **16**(3), 619–624 (2013).

[7] Anwar, M., Sabry, Y., Basset, P., Marty, F., Bourouina, T. and Khalil, D., "Black silicon-based infrared radiation source," Silicon Photonics XI **9752**, 97520E (2016).

[8] Sabry, Yasser M; Khalil, Diaa; Bourouina, Tarik E; Anwar, M., "Structured silicon-based thermal emitter," US Patent Application Number 9,793,478 (2017).

[9] Charles R. Shipley, Jr. Newton; Lucia H. Shipley, Newton; Michael Gulla, Newton; Oleh B. Dutkewych, Medfield, all of mass, "Electroless copper plating," US Patent Application Number 3,615,733 (1971).

[10] Dos Santos Filho, S. G., Pasa, A. A. and Hasenack, C. M., "A mechanism for electroless Cu plating onto Si," Microelectron. Eng. **33**(1–4), 149–155 (1997).

[11] Han, X., Wu, W., Li, Y., Li, Z., Hao, Y. and Yan, G., "Electroless copper plating applicable for bulk-silicon micromachined radio frequency inductor," Thin Solid Films **515**(4), 2607–2611 (2006).

[12] Rehman, A. and Lee, S. H., "Review of the potential of the Ni/Cu plating technique for crystalline silicon solar cells," Materials (Basel). **7**(2), 1318–1341 (2014).

[13] Kim, D. H. and Lee, S. H., "Investigation on plated Ni/Cu contact for mono-crystalline silicon solar cells," Electron. Mater. Lett. **9**(5), 677–681 (2013).

[14] Liu, X., Coxon, P. R., Peters, M., Hoex, B., Cole, J. M. and Fray, D. J., "Black silicon: Fabrication methods, properties and solar energy applications," Energy Environ. Sci. **7**(10), 3223–3263 (2014).

[15] Bühler, J., Steiner, F. P. and Baltes, H., "Silicon dioxide sacrificial layer etching in surface micromachining," J. Micromechanics Microengineering **7**(1) (1997).

[16] Schlesinger, M., Modern electroplating, Wiley, Hoboken, NJ, 1-66 (2010).

[17] Nagahara, L. A., Ohmori, T., Hashimoto, K. and Fujishima, A., "Effects of HF solution in the electroless deposition process on silicon surfaces," J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. **11**(4), 763–767 (1993).

[18] Eltagoury, Y. M., Sabry, Y. M. and Khalil, D. A., "All-Silicon Double-Cavity Fourier-Transform Infrared Spectrometer On-Chip," Adv. Mater. Technol. **4**(10), 1–6 (2019).

[19] Region, N., "2016 , 33 rd NATIONAL RADIO SCIENCE CONFERENCE On the Environmental Gas Sensing Using MEMS FTIR Spectrometer in the 2016 , 33 rd NATIONAL RADIO SCIENCE CONFERENCE," 348–355 (2016).

[20] Erfan, M., Elsayed, A. A., Sabry, Y. M., Mortada, B., Sharaf, K. and Khalil, D., "Environmental mid-infrared gas sensing using MEMS FTIR spectrometer," MOEMS Miniaturized Syst. XVI **10116**, 101160L (2017).