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Laser Processed Micro-Groove based Black Si

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Abstract. In this work we have reported generation of Black Silicon (Si) consisting of micro-groove structures. These micro-groove structures were produced on the monocrystalline Si surface by using 532-nm-wavelength nanosecond laser of 40 KHz repetition rate and 2 ns pulse duration. Field emission electron microscopy is done to characterize the morphology of the generated micro-groove structures. The reflectance of the Si surface containing these structures was measured by using a spectrophotometer attached with an integrating sphere within the wavelength range of 300-800 nm. From this study we found that the surface reflectance is reduced up to 4.5%. This significantly low reflectance of the Black Si surface makes them suitable for solar cell development application. The reported method for reduction of reflectance involves a single step dry etching process and is more advantageous to other methods in terms of less time consumption, reduced number of processing steps and costs effectiveness. Detail discussion is given on this regard.

INTRODUCTION

The capability of light absorption of a solar cell is significantly enhanced when its surface is rough or textured instead of smooth. In such textured Si surface the reflectivity is reduced drastically so as to provide this higher absorption of incident solar radiation resulting in higher efficiency of the solar cell. Such types of Si are called as Black Si [1]. Particularly the reduction of front surface reflection for Black Si based solar cell is most effective to enhance the current efficiency. The surface texturization in Black Si can be done by three methods viz (i). Wet etching or Acid etching method, (ii). Dry etching method and (iii). Bottom up nanostructures growth method. Wet etching or Acid etching such as electrochemical etching [2], stain etching [3], metal assisted chemical etching [4], is a process for removal of materials by using chemical solutions that remove unwanted materials from a wafer. The merits of wet etching processes are high selectivity, simple equipment and high etching rate. Still wet etchings have many demerits. Firstly, it is generally difficult to control. Secondly, wet etching requires large amount of chemical solutions so that the substrate material will be completely within the etchant chemical solution. Thirdly, the etchant chemicals must be constantly changed to maintain the equal etching rate throughout. Due to these reasons the chemical and removal costs connected with wet etching are tremendously high [5, 6].

Dry etching process such as, physical dry etching, chemical dry etching, plasma etching [7], gas etching, and physical-chemical etching. Physical dry etching process needs high kinetic energy (ion, electron, or photon) beams to etch off the substrate atoms. Chemical dry etching is known as vapor phase etching [8, 9], where no chemical solutions are used for this etching process. In this process the chemical reactions will be occurred between the molecules, atoms or ions of the gas etchant and the materials which are to be removed. The chemical dry etching process is generally isotropic and shows high selectivity [10]. Reactive ion etching [11] based Black Si surface was first demonstrated by Jansen et. al. [12]. In this etching process the surface of the sample contains needle like rough

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surface on which the lithography printing is very difficult which is essential subsequent step of solar cell development. This problem may be overcome followed by the chemical wet etching step. However, this is a major drawback in this etching process where, using of chemical solution is the additional step for reduction of reflectance [13]. The effective and operative texturization can be done mechanically, but it has some restrictions for the textured materials. This mechanical texturization process cannot be applicable for thin, wrapped and fragile material like Si [14, 15]. Black Si can also be generated with bottom up grown nano structures. The defined method used for this bottom up growth method are vapor solid liquid method [16], chemical vapor deposition etc. However, such growth methods suffer from the limitation like slow growth rate, relatively high costs and non-reproducibility.

Use of laser is an advanced and promising technique for Si surface texturization. It is a very optimized and contactless technique and has several advantages like (i) the different types of texture patterns can be created directly with very less number of steps, (ii) well controllable, (iii) reproducible and (iv) can be adopted for all types of Si. Several works have been carried out using this technique to reduce the reflectance of single crystalline, multicrystalline and amorphous of bulk and thin film of Si [17-24]. However, in these works self generated or self organized laser induced periodic structures (LIPS) and the micro or nano conical structures are reported to be responsible for reduction of reflectance. Generation of such structures generally require very precise control of fluences and pulse number hitting the sample and also time consuming. In contrast to this, here we demonstrated that micro-grooves are generated by a single step processing with 532 nm nanosecond laser can also produce Black Si. The advantages of the present method are discussed.

EXPERIMENTAL DETAILS

Growth of Micro-Grooves

The schematic diagram of the laser processing experimental set up is shown in the Fig. 1. The second harmonic radiation of a linearly polarized Nd: YAG laser was used to carry out this experiment. The wavelength, duration and repetition rate of the laser pulses are 532 nm, 2 ns and 40 KHz respectively. The laser beam was focused by a Plano-convex lens of focal length of 100 mm on to the monocrystalline silicon sample. The sample was placed at the focal plane of the lens and the spot size (waist, ω_0) of laser beam on its surface was 50 µm.

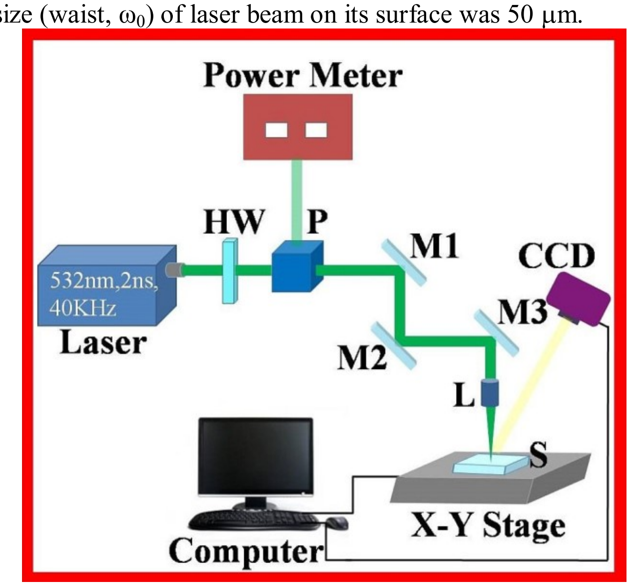

FIGURE 1. Schematic of experimental setup (HW = Half Wave plate, P=Polarizer, M1, M2, M3= Mirrors, CCD = Charged Coupled Device, L = Lens, S = Sample).

For the large area processing, the sample was mounted on a motorized x-y stage (X-XY-LSM025A-KX13A-SQ3, Zaber technologies Inc) which was given a raster scan by using an indigenously developed LabVIEW software program. The laser fluence was controlled by a half wave plate (HW) and a polarizer (P). The beam reflected by polarizer was measured continuously by a power meter. A Charged Coupled Device (CCD) camera is used to capture the real time monitoring of the laser material processing. All the laser processing work was done in the air medium. Sequential micro-grooves were engraved with constant and specified space in the successive texturing of the surface.

Characterization of the Micro-Grooves

The morphological study of the generated micro-grooves was done by using Field Emission Scanning Electron Microscope (FESEM, JEOL). The reflectance was measured by using a spectrophotometer (UV-2450, SHIMADZU) attached with an integrating sphere within the wavelength range from 300 nm to 800 nm.

RESULTS AND DISCUSSION

The FESEM image of the processed region of Si is shown in Fig. 2(a). In our experiment, total 1x1 cm^2 area was textured with the processing step of 300x300. In this type of processing the stage moves in a step size of 33 µm. This leads to grating structures of period 33µm along with micro-groove matrix of spacing ~33 µm whole across the processed region. This happens due to the slowing down of the scanning velocity after each 33 µm of stage movement (and hence hitting of more number of pulses in those regions).

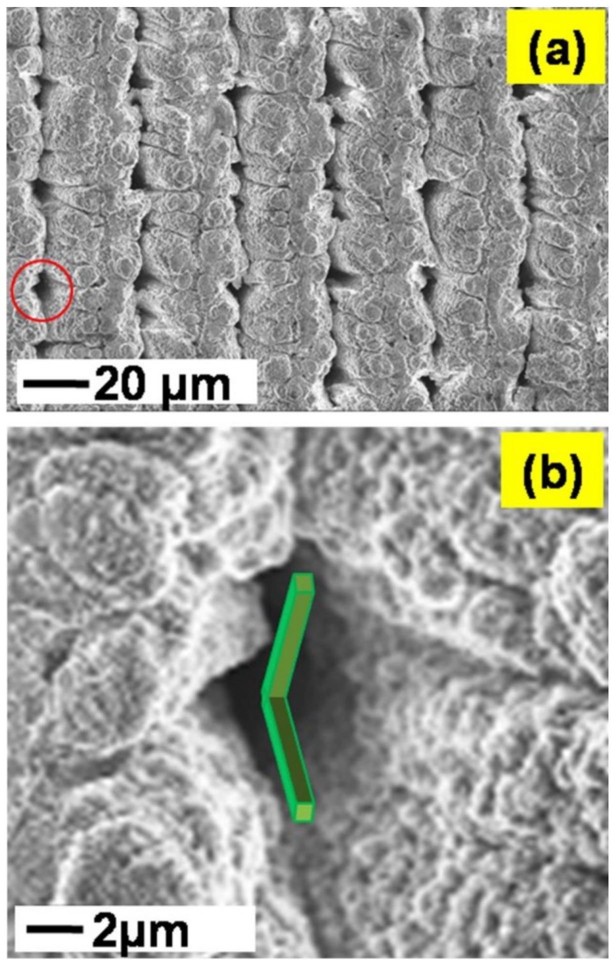

FIGURE 2. FESEM images of the laser processed region (a), one of the micro-groove (b).

The magnified image of one of these micro-grooved structures is shown in Fig. 2(b). From this image it appears that the average size of these grooves are ~7 µm with V-like asymmetry in most of the cases. The diffused reflectance of the Si surface containing the above mention micro-groove is shown in Fig. 3. This figure indicates that the reflectance decreases down to 5.5- 4.5% within the wavelength range of 300 nm to 800 nm. It is to be mentioned here that, the polished Si showed much higher reflectance (50-45 %) in this wavelength region. This indicates that, in the present case Black Si (i.e. Si surface with significantly low reflection) has been generated.

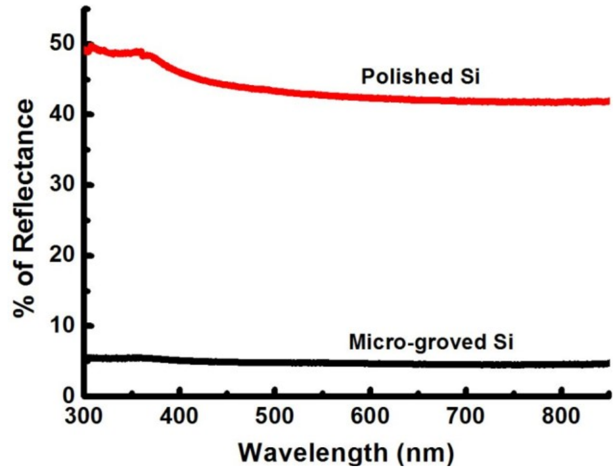

FIGURE 3. Reflectance of polished Si surface and Black Si surface containing laser processed micro-groove structures.

Previously several works have been done on reduction of reflectance using micro-grooves [25-28]. Abouelsaood et. al., theoretically demonstrated that this reduction is possible by using the micro-groove [25]. Experimentally the best result on reduction of reflectance (R_{avg}= 3.3 %) through micro-groove has been demonstrated by Choi et. al [27]. So the reduction of reflectance demonstrated in the present work is comparable to the result obtained by them. However, it is to be mentioned here that the micro-grooves reported by them were fabricated by UV laser processing followed by chemical etching. On the other hand the present process is based on only a single laser processing step (i.e. no chemical etching step), so the method is much simpler than the method demonstrated by them.

Further, it is to be noted here that the 532 nm and 355 nm laser radiations are generally generated through the nonlinear optical frequency conversion process like second harmonic generation (SHG) and third harmonic generation (THG) respectively of the solid state laser of wavelength 1064 nm. The SHG process is generally simpler and more efficient than the THG process therefore the laser system that we have used to generate the micro-grooved based Black Si is simpler and cost effective than the system used by Choi et. al. to achieve similar goal.

CONCLUSION

The micro-groove grating structures were produced on the monocrystalline silicon surface by using 532-nm wavelength nanosecond laser of 40 KHz repetition rate and 2 ns pulse duration. From the reflectance study it was found that the surface reflectance is reduced up to 4.5%. This significantly low reflectance of the Si surface makes them suitable for solar cell development application. The generated Black Si can also found to be suitable for surface enhanced Raman Spectroscopy (SERS) application The reported method for reduction of reflectance involves a single step dry etching process and comparatively superior to the other reported micro-grooves based methods in terms of reduced number of processing steps and costs effectiveness.

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