Formation of "Black Silicon" on a Surface of Ni/Si Structure by Nd:YAG Laser Radiation

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Abstract:

We have shown the possibility to form a new type of material known as "black silicon". After irradiation of a Si sample surface, covered with 30 nm thick Ni layer, by Nd: YAG laser beam at intensity 4.5 MW/cm^2 the "black silicon" was formed. The formation and self-organization of cone-like microstructures on the Ni/Si surface has been detected by scanning electron microscope (SEM). Light is repeatedly reflected between the cones in the way that most of it is absorbed, therefore the surface becomes like a "black body" absorber. The micro-chemical analysis performed on SEM has shown that the microstructures contain $NiSi_2$. This was approved by presence of LO phonon line in Raman back scattering spectrum. The control of micro-cone shape and height was achieved by changing the laser intensity and number of pulses.

Keywords: *"black silicon", self-organization, microstructures, Nd: YAG laser.*

1. Introduction

"Black silicon" [1] is a new type of material, which absorbs from 96% to 98 % of the incident light generating hundreds times more current than ordinary Si (60%). Therefore it can be an excellent material for solar cell production [2]. In addition this material could be also used in infrared detector production - a novel application of Si. Single crystal Si is transparent for infrared radiation, but "black silicon" is able to absorb it .The surface micro structuring of Si by femtosecond laser induced plasma [3] or chemical vapor deposition with catalytic metal on Si [4] is used for "black Si" formation. We propose another method - the micro-cone formation by the irradiation of Ni/Si layer structure by basic frequency of microsecond Nd:YAG laser.

2. Experiment

To produce a sample of 30 nm nickel film of the 99.99 % purity has been deposited onto the Si substrate by DC magnetron sputtering method at room temperature. Before the sputtering the surface of Si was subjected to ion cleaning in Ar ambient. Afterwards the Ni/Si layered structure was exposed to the microsecond Nd:YAG laser beam at basic frequency, various threshold intensities and pulse numbers in a scanning mode.

The structural and optical characteristics of microcones where studied by scanning electron microscopy (SEM) and Raman spectroscopy. SEM measurements were performed on the Carl Zeiss LEO 1455 VP device with Rontek EDXA attachment that have also allowed analyze the composition of the sample. Raman spectra of the Ni/Si sample were obtained in the various configurations, including a backscattering mode, using the laser excitation wavelength of 532 nm at room temperature. The spectral resolution was 1 cm^{-1} and the beam diameter on the sample surface was about 1 mm.

3. Results and Discussion

Fig. 1 presents Ni/Si surface subjected to laser irradiation at different conditions. After Ni/Si structure irradition by Nd:YAG laser beam a various degree of damage is observed on the surface of the Ni/Si layered system such as the appearance of cracks and formation of regular cone-like structures. At the lowest intensity and number of laser pulses applied, the surface of Si is stongly cracked and nickel is present in the form of drops. The average drop size is about 0.5-0.8 µm and they are quite evenly distributed off the zones, where microcones are formed. Microcones appear not on a regular basis and their sizes vary from a tiny of 10 mm up to a bigger ones of 40 µm. The surface of microcones is covered with net dendride

(a) (b) (c)

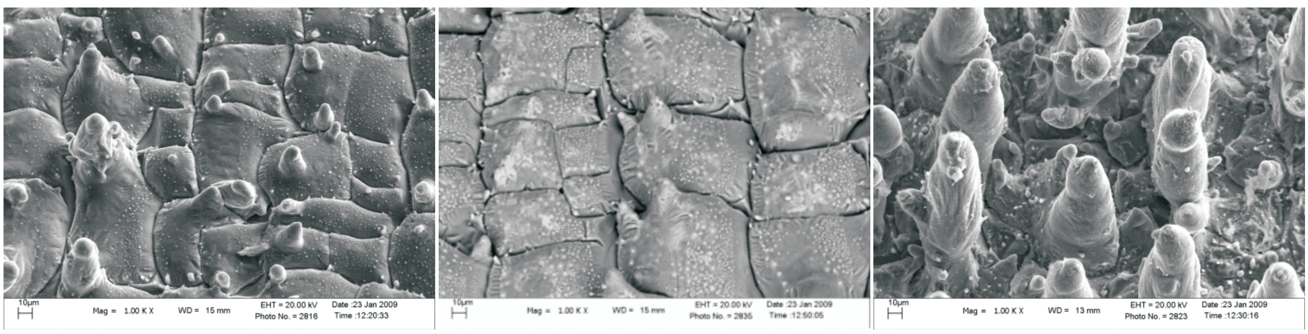

Fig. 1. SEM image of Ni/Si surface irradiated by Nd:YAG laser at intensity 3.15 MW/cm^2 a) about 3 laser pulses per point, and at intensity 4.5 MW/cm^2; b) about 10 laser pulses per point, c) about 22 laser pulses per point.

structures. The Nd:YAG laser intensity threshold at which the self-organization of cone-like microstructures was observed on the surface of Ni/Si layer system was 3.15 MW/cm^2. The control of micro-cone shape and height was achieved by changing the intensity of laser radiation and a number of pulses. The increase of the laser intensity up to 4.5 MW/cm^2 and number of pulses from 3 up to 10 does not result in the appearance of more microcones although the redistribution of nickel can be observed. The nickel net covering the microcones is moved up the cone side, leaving the bottom of the cone without any nickel. The further increase of the laser intensity and number of pulses leads to the formation of cone-like microstructures with most of Ni on the top of the cone and maximal height of the cone about 80-100 μm (Fig.1). The irradiated region of the structure with maximal intensity 4.5 MW/cm^2 and 22 pulses becomes black (Fig.1). Moreover we can notice that microcones appear regularly and mostly of the same shape and height. No dendrite structure is found on the surface of microcones, the cone side is pure Si.

During the research of the irradiated sample surface by SEM the "metallic islands" with a diameter less than 1 μm have been found. The micro-chemical analysis by means of energy-dispersive X-ray attachment has shown that these islands consist of pure Ni or Ni and Si composition $NiSi_2$. It means that it is possible to form the new phase $NiSi_2$ in our experiment. We assume that $NiSi_2$ is formed *via* melting and recrystallization of a part of Si substrate. A one more evidence of $NiSi_2$ formation is the appearance of a phonon line at 225 cm^{-1} which is attributed to Ni-Si vibration in Raman back scattering spectrum (Fig.2). We eliminate the possibility of NiSi phase formation as Ni-Si vibrations for NiSi posses at least two characteristic first-order peaks at 196 and 214 cm^{-1} [6]. At the same time slight oxidation of the structures is found after laser irradiation in comparison with untreated samples and the most oxidized regions follow $NiSi_2$ formation.

4. Model of micro-cone formation

Proposed mechanism of micro-cone formation is explained by two steps. In the first step Ni film melts after irradiation by laser beam and the influence of surface tension forces leads to Ni "metallic island" formation. At higher laser beam intensities islands transforms in to sphere-like particles containing Si and Ni. In the second step - Si melts outside each island, evaporates, accumulating on Ni and after diffusion through Ni causes micro-cone growth [5].

5. Conclusion

We have demonstrated the possibility to form the "black Si" on the surface of Ni/Si structure by Nd:YAG laser radiation. The shape and height of micro-cone structure strongly depends on Nd:YAG microsecond laser intensity and number of laser pulses, that allows controlling this parameters. We have found that microcones are formed as a regular structure at the laser intensity and number of pulses leads to the formation of cone-like microstructures It was found that it is possible to form a silicide phase, namely $NiSi_2$, on the Si surface by Nd:YAG laser radiation.

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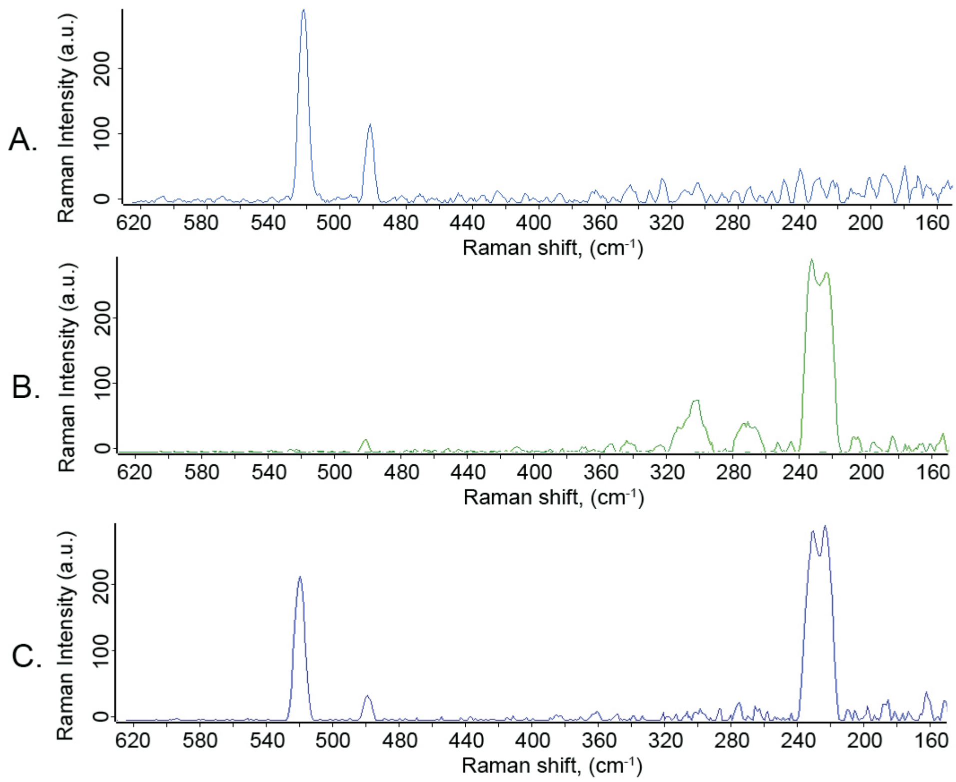

Fig. 2. Raman spectrum of the Ni/Si sample surface irradiated by Nd:YAG laser: A. - 4.5 MW/cm^2, 10 laser pulses; B. - 3.15 MW/cm^2, 3 laser pulses; C. - 4.5 MW/cm^2, 22 laser pulses.

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