Structure of silicon nano- and microparticles obtained by electric-spark dispersion method

Sergiienko R. A.[1], Ilkiv B. I.[2], Petrovska S. S.[2], Lopatko K. G.[3], Lopatko S. K.[3], Vinarchuk K. V.[3], Verkhovliuk A. M.[1], Zaulychnyy Ya. V.[4]

[1] Physico-Technological Institute of Metals and Alloys of the NAS of Ukraine, 34/1, Vernadsky Ave., Kyiv, 03142, Ukraine,
e-mail: rsruslan17@gmail.com
[2] Frantsevich Institute for Problems of Materials Sciences of the NAS of Ukraine, 3, Krzhyzhanovsky Str., Kyiv, 03142, Ukraine.
[3] National University of Life and Environmental Sciences of Ukraine, Heroyiv Oborony st., 15, Kyiv-03041, Ukraine,
e-mail: date01092015@ukr.net
[4] National Technical University of Ukraine "Kyiv Polytechnic Institute", Engineering-physical Faculty, 35 Polytekchnichna Str., Kyiv 03056, Ukraine.

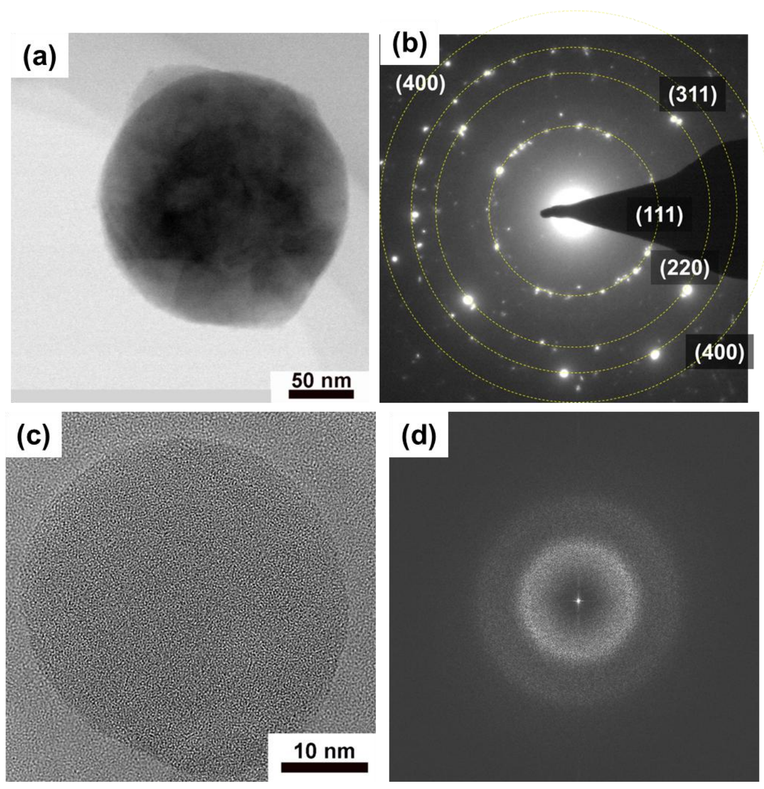
Introduction

Silicon nanoparticles have been attracting a lot of attention lately as they demonstrate important properties for their technological application as a deoxidizer in steelmaking, alloy manufacturing, in the semiconductor industry, in biology and medicine, for lithium-ion batteries, in optoelectronic devices, in agriculture, etc. [1-3]. It is widely known that the study of the electronic structure of solids performs a very important task in predicting their physicochemical properties. Although the electronic structure of silicon has been studied extensively [4], much less work has been devoted to the study of it in nanoscale silicon particles [5]. In this work powder sample of silicon nano- and microparticles obtained using **electric-spark dispersion (ESD) method** of silicon electrodes and silicon granules in 40 % solution of methyl alcohol in water were investigated by ultrasoft X-ray emission spectroscopy **(USXES)**, photoelectron spectroscopy **(XPS)**, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. It was found that the surfaces of particles obtained in a solution of alcohol in water are covered with silicon oxide and chemisorbents, while the core consists of crystalline silicon.

Methods

SiLα X-ray emission spectra correspond to transitions of 3d3s → 2p. SiLα X-ray emission spectra were obtained by ultra-soft X-ray emission spectroscopy **(USXES)** using a PCM-500 X-ray monochromator (Burevestnik, St. Petersburg, Russian Federation). Measurements were carried out at a pressure in the working volume of the spectrometer 2.67×10^{-4} Pa. Additionally, the electronic state of silicon atoms was investigated by X-ray photoelectron spectroscopy (**XPS**, PHI 5600). AlKα radiation (E = 1486.6 eV) was used as the source of XPS radiation excitation. Silicon nanoparticles were obtained using an electric-spark dispersion **(ESD)** unit from silicon granules of technical purity (99.9%) in 40% solution of methyl alcohol in water. A voltage of 30 – 160 V was applied to the silicon electrodes with the duration of discharge pulses from a few microseconds to milliseconds and the frequency of electrical pulses was 100 Hz, the power of the installation – 0.5 kW.

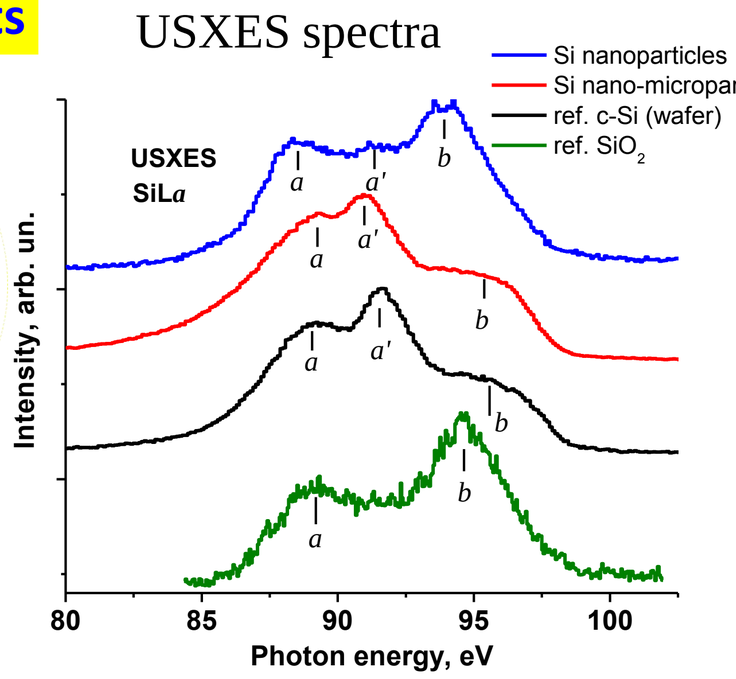
Results



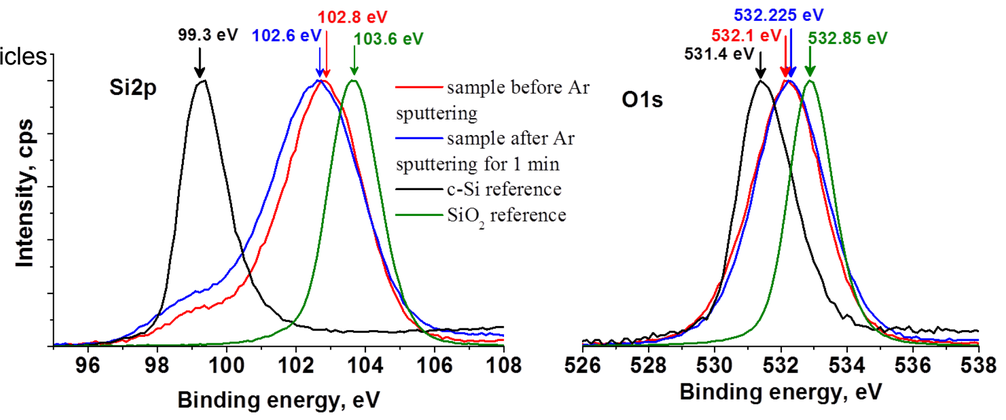
(a), (c) Bright-field TEM images of silicon nanoparticles synthesized by the ESD method in a solution of 40% methyl alcohol in water. **(b)** The electron diffraction pattern of the Si nanoparticle shown in Figure-image (a). **(d)** The Fast Fourier transformation (FFT) analysis of silicon nanoparticle shown in Figure-image (c).

The synthesized Si nano- and microparticles have almost spherical shape with a wide size distribution from 15 nm to 10 µm. Si nano- and microparticles have a cubic face-centered structure (fcc, Fd3m) and some nanoparticles showed amorphous structure, this fact was confirmed by FFT analysis.

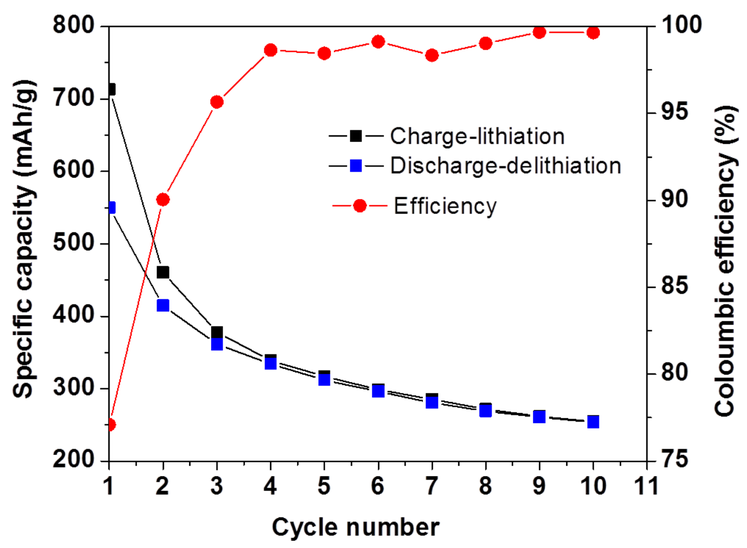
USXES spectra



XPS spectra



USXES SiLα X-ray emission and XPS spectra of prepared powder samples (blue and red lines) in comparison with reference spectra of semiconducting silicon wafer (c-Si) (black line) and pyrogenic silicon dioxide SiO_2 (green line) with amorphous structure.



Specific charge capacity and coulombic efficiency of an electrode (anode) made from Si nano- and microparticles powder sample mixed with graphite powder purchased from Wako in a three electrode cell. Cycling was carried out at room temperature in a voltage range of 0.0–2.0 V (versus Li/Li^+) at a rate of 0.01 C (current density of 7.2 mA/g).

Conclusions

XPS studies showed a high degree of oxidation of the surface of silicon nanoparticles and the presence on the surface of nanoparticles of oxygen-containing complexes with different charges of oxygen ions, which is also confirmed by USXES SiLα X-ray emission spectra and electron mapping analysis. Synthesized Si nano- and microparticles mixed with graphite powder showed a low electro-chemical performance-quick degradation of specific capacity from 550 mAh/g at 1st cycle to 254 mAh/g at 10th cycle during discharge of cell.

References

[1] Gribov, B. G., Zinov'ev, K. V., Kalashnik, O. N., et al., **2017**. Production of Silicon Nanoparticles for Use in Solar Cells. *Semiconductors*, 51, pp. 1675–1680.
[2] Rastogi, A., Tripathi, D.K., Yadav, S., et al., **2019.** Application of silicon nanoparticles in agriculture. *3 Biotech*, vol. 9, No 90, pp. 11.
[3] Wang J., Huang W., Kim Y. S., et al., **2020.** Scalable synthesis of nanoporous silicon microparticles for highly cyclable lithium-ion batteries. *Nano Research,* vol. 13, № 6, pp. 1558-1563. **[4]** Kurmaev, E.Z., Galakhov, V.R., Shamin, S.N., et al., **1997.** Local structure of porous silicon studied by means of X-ray emission Spectroscopy. *Appl. Phys. A*, 65, pp. 183–189. **[5]** Guzmán-Verri, G.G., Lew Yan Voon, L.C., **2007.** Electronic structure of silicon-based nanostructures. *Phys. Rev. B*, 76, pp. 075131.