

Surface Chemistry of Butyl-Passivated Silicon Nanoparticles Studied by Synchrotron-Radiation Photoelectron Spectroscopy

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Various Si-based nanostructures have a great interest, since it has been reported that they show a strong photoluminescence, and therefore there is a possibility of future integrating electronic devices with optical sensing technique. Numerous works focused on the optical properties of Si nanoparticles prepared by various methods have been reported to date. However, data in the literatures are not universally accepted, and depend on various factors in the individual samples. Especially, the physical and chemical properties of nanoparticles are greatly influenced by surface chemical states due to the large surface to volume ratio with decreasing the size to the nanometer scale. In this work, we have synthesized n-butyl-passivated Si nanoparticles with well crystalline nature and well surface-passivated surface by the solution routes, and have directly characterized their electronic structures in the vicinity of Fermi level using synchrotron-radiation photo-electron spectroscopy. Furthermore, we have compared the valence-band photoemission spectra of fully n-butyl-passivated Si nanoparticles and those with oxygen contaminants in order to directly investigate the effect of surface chemical nature on their electronic structures.

Figure 1 shows the synchrotron-radiation valence-band photoemission spectra of as-prepared n-butyl-passivated Si nanoparticles with $d_c = 1.1$ nm and those exposed to ambient air for 10 min, on the HOPG substrate at room temperature with photon energy of 195 eV. The spectral features around 7 and 5.5 eV binding energies in the photoemission spectrum of as-prepared n-butyl-passivated Si nanoparticles originate from the C 2p derived states. The spectral feature around 7 eV binding energy originates from the C–H bonds in the butyl surface-passivants, and that around 5.5 eV binding energy originates from the Si–C bonds between the Si nanoparticle and butyl surface-passivants. This spectral feature around 5.5 eV in binding energy indicates that the present Si nanoparticles are well surface-passivated by butyl molecules. The spectral feature around 13.5 eV binding energy originates from the C 2s-derived states. The other spectral features around 3.5, 9, and 11 eV in binding energies originate from Si 3s- and 3p-derived electronic states. On the other hand, the valence-band photoemission spectrum of n-butyl-passivated Si nanoparticles with $d_c = 1.1$ nm after exposure to ambient air for 10 min is similar to that of as-prepared n-butyl-passivated Si nanoparticle. However, the spectral intensity derived from Si–C bonds around 5.5 eV binding energy

decreases with oxygen contaminants. This clearly indicates the removal of the surface-passivants of butyl molecules and subsequent contamination of oxygen. It should be noted that the valence-band photoemission spectrum of n-butyl-passivated Si nanoparticles with oxygen contaminants exhibits an additional feature centered around 2.6 eV binding energy (shown by the arrow). Puzder *et al.* have previously reported the Density of State (DOS) of hydrogen-passivated Si nanoparticles with various contaminants by means of local density approximation (LDA) in order to see physical origin of the effect of oxygen on the gap. [1] When a double bonded contaminant such as oxygen and sulfur is added to Si nanoparticles, the Si sp_3 network is considerably distorted and the HOMO and LUMO change their nature significantly. As a result, HOMO and LUMO states localized in the vicinity of the Si=O double bond, and the modified DOS originated from the HOMO and LUMO appears near the Fermi level as the additional features. From the comparison with this LDA theoretical DOS, it is concluded that this additional feature is ascribed to oxygen-contaminants-induced states, and this result provides a direct evidence of the effect of oxygen contaminants on the electronic structure that the previous calculation has predicted.

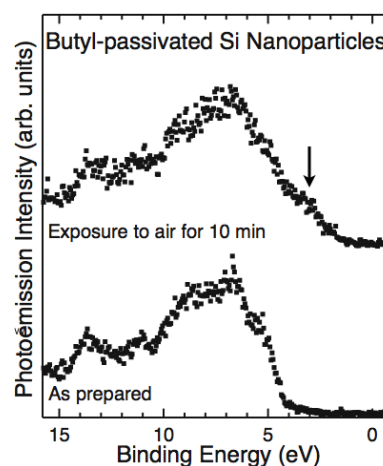


Figure. 1 Valence-band photoemission spectrum of as-synthesized n-butyl-passivated Si nanoparticles with $d_c = 1.1$ nm and those exposed to air for 10 min. The arrow indicates the additional feature originated from the oxygen-contaminant-induced states.

[1] A. Puzder, A. J. Williamson, J. C. Grossman, and G. Galli, *Phys. Rev. Lett.*, **88**, 097401 (2002).