Preparation and Surface Layer Modification of Silicon Nanoparticles Dispersed in 2-Propanol *

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Silicon nanoparticles dispersed in 2-propanol were prepared by using an arc plasma with gas flow method in a new designed home-made apparatus. The particles are composed of silicon crystal core covered by oxidized amorphous silicon shell. The composition of the particle surface layer can be modified by preparing the sample in different atmosphere. The particles can be also obtained with different core composition and different size which we need.

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Preparation, structures, and properties of nanosilicon such as porous silicon, silicon particles, silicon particles embedded in other materials, and silicon colloids have attracted much attention because these materials have efficient luminescence in the visible region even at room temperature.[1-3] The surface layer of luminescent silicon nanocrystallites is usually covered by silicon oxyhydrides[4-6] or silicon oxide,[7,8] which makes the electronic properties of the surface layer differ from those of the crystalline silicon core. This indicates that the oxygen and/or hydrogen in the surface layer of those kinds of materials plays a very important role for the luminescence in visible region. Several methods, such as the chemical method, the electrochemical method, and the inert gas evaporation method, have been used to prepare nanometer-sized silicon.[2,3,9] Each method has its own advantages. However, they have some limitations. For example, the impurity of the particles is high because of the source of the residual chemical matter or the heating boat, and the composition of the particles is not easy to control. In this letter we present the results of silicon nanoparticles dispersed in 2-propanol (silicon nanocolloids) prepared by using an arc plasma with gas flow method in a new designed home-made apparatus. The method has no contamination source of the residual chemical matter or the heating boat, and the particle composition of the surface layer and the core can be easily modified. Sample was characterized by a transmission electron microscope (TEM, Hitachi H-8100), an energy disperse x-ray (EDX, Kevex) analysis, and by a Fourier transform infrared (FTIR, FT-210, Horiba) spectrophotometer.

Figure 1 shows a schematic diagram of the apparatus. In the colloid preparation process, briefly, the vacuum chamber was evacuated first, the cold trap was installed far away from the arc plasma chamber and cooled by liquid nitrogen, and solvent was introduced onto the cold trap to form a cryogenic matrix. Then, the discharge gas was introduced and the normal discharge process was started. Through the anode, the particles were trapped on the frozen solvent directly. After enough amount particles were accumulated, the discharge process was stopped, the Ar gas was introduced into vacuum chamber to reach atmosphere pressure, and the frozen solvent was melted. In this way, we can separate the discharge zone from particle trapping zone to avoid the reaction of the high temperature particles with solvent. Finally, through the Septum rubber seal, the silicon colloids were sucked into a glass stock bottle with a Laura-lock syringe anaerobically. In this experiment, the discharge gases were research grade Ar and $Ar + H_2$ (2:1), the solvent is 2-propanol and the purity of the silicon target was 99.9999%. The background vavuum of the system was about 4 Pa, the discharge gas pressure was about 100 Pa, the voltage applied was 15 V. In order to separate the very large particles, all the samples were filtered by using the filter paper of the pore size of 300 nm.

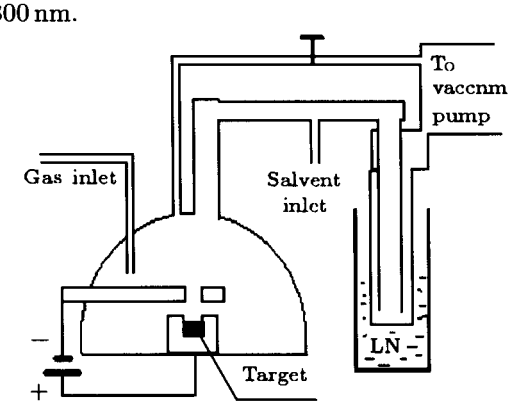

Fig. 1. Schematic diagram of the apparatus.

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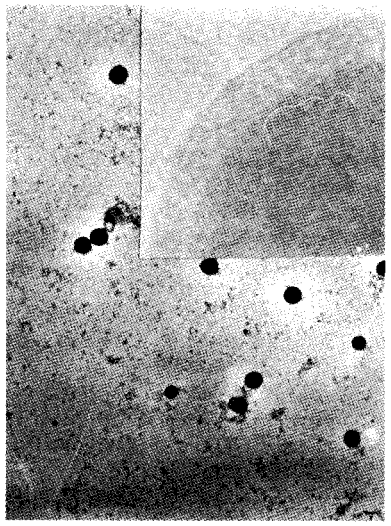

Fig. 2. Low magnification TEM micrograph of the particles of the sample prepared in Ar atmosphere. The inserted high magnification TEM micrograph is a part of a typical particle. Lattice image is from (111) plane of the silicon crystalline (spacing of 0.31 nm).

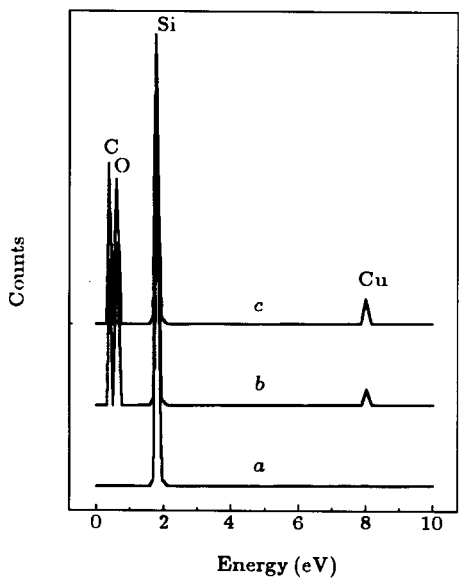

Fig. 3. EDX analysis with fine mode (the electon beam size is 7 nm). Spectrum of the particle center (curve *a*), spectrum of the particle edge (curve *b*), and spectrum of very small particles (curve *c*).

TEM observation shows that the particles are separated and spherical in shapes. Most of them are less than 100 nm in diameter (about half of them are less than 10 nm). There are two kinds of particles: One is the ensemble of very small silicon particles in the region of a few of nanometer, the other is large silicon particles in the region of a few tens to a few hundreds of nanometer. These two kinds of particles are composed of silicon crystal core covered by oxidized amorphous silicon shell, which was also confirmed by EDX. Figure 2 is the low magnification TEM micrograph of the particles of the sample prepared in Ar atmosphere (the same TEM results were obtained from the sample prepared in $Ar + H_2$ atmosphere). The inserted high magnification TEM micrograph is a part of a typical particle. It clearly shows lattice structure in the particle center [lattice image is from (111) plane of the silicon crystalline (spacing of 0.31 nm)] and amorphous structure on the particle edge. Figure 3 is the EDX spectra of the sample prepared in Ar atmosphere. Curves $a-c$ in Fig. 3 are the EDX spectra of the center of a large particle (curve *a*), particle edge (curve *b*), and of very small particles (curve *c*) using an electron beam size of 7 nm (the EDX results for the sample prepared in $Ar + H_2$ atmosphere are almost the same except the intensity of oxygen peaks is lower than that of the sample prepared in Ar atmosphere). The oxygen peak appeared in the spectra of the particle edge and disappeared in the spectrum of the particle center (the Cu and C peaks are from carbon film covered TEM copper sample grid). The particle surface layer is oxidized because of the low background vacuum and a very high temperature during the preparation process. The oxidized surface layer of the particles was thought to be formed during the discharge process through the chemical reaction of the silicon atoms with the residual oxygen in the vacuum chamber. After the preparation process, the produced samples are in colloidal state in which silicon particles are dispersed in 2-propanol solvent. Therefore, further air oxidation can be avoided while the colloid is kept in a storage bottle.

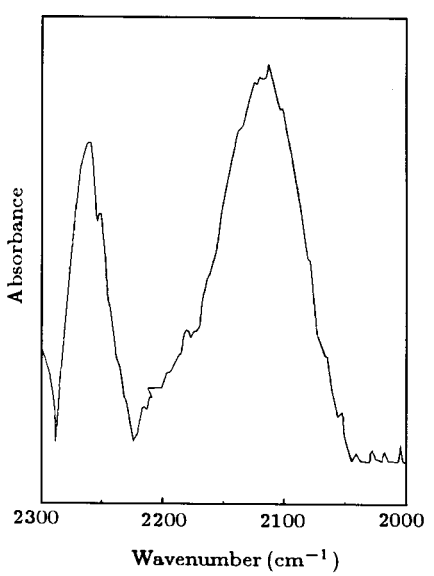

Fig. 4. IR results in the region of 2000–2300 cm^{-1} for the sample prepared in $Ar + H_2$ atmosphere.

As hydrogen cannot be detected by EDX analysis, the sample prepared in $Ar + H_2$ atmosphere was also measured by FTIR spectrophotometer. There

are two peaks in its IR spectra in the region of $2000-2300\,cm^{-1}$ which are of the Si−H−Si stretching vibration[10] (see Fig. 4). This indicates there exists hydrogen in the particles. Based on these IR results and the TEM results of the particle structures (especially, the lattice images), which are the same for samples prepared in both Ar and $Ar + H_2$ atmospheres, we can conclude that hydrogen and oxygen only exist in the surface layer of the particles. Therefore, the surface layer composition of the particles can be modified by preparing the sample in different atmosphere. The silicon nanoparticles with different size were obtained by filtration and ultrafiltration methods for colloids.[11] The $Fe_{0.42}Si_{2.67}$ crystal nanoparticles covered by very thin oxidized amorphous silicon shells were also produced by the same preparation method with the raw materials of Si:Fe(3:1).[12] Combining this preparation method with filtration and ultrafiltration methods, we can obtain the nanoparticles with different surface layer composition, different core composition, and different size which we need.

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