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Functionally graded nanocrystalline silicon powders by mechanical alloying

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ABSTRACT

Functionally graded nanocrystalline silicon powder, having varied bandgap. has been prepared using mechanical alloying technique. The solar grade (99.999% pure) nanocrystalline silicon (nc-Si) powder was ball milled in argon atmosphere in an attrition mill for 4 h to 20 h (4 h, 12 h and 20 h) to reduce crystallite size in it. The milled powder samples were then degassed, to remove entrapped gases, in a vacuum of 10^{-2} torr at 200 °C for 1 h. Transmission electron microscopy and X-ray diffraction studies show the crystallite size of all the powders are in the nanometer range and decrease in crystallite size was seen with increasing milling time. Raman spectroscopy shows nanocrystalline phases in the milled powder particles with 100% crystalline volume fraction. UV–Vis-IR spectroscopy was used to determine bandgap of the powder samples using Tauc formula. The bandgap and crystallite size in silicon powder is found to be the function of milling duration, without addition of any alloying element. The nc-Si powder with different bandgaps may find potential applications in the field of functionally graded solar cells.

1. Introduction

Silicon is an IV group element of the periodic table which has been attracting researchers for several years in the field of semiconductors (bandgap 1.12 eV) due to its large abundance. In recent years, nanotechnology allowed researchers to play with bandgap of silicon, as bandgap of semiconductor nanomaterials is a function of particle or crystallite size. Such semiconductor nanomaterials have vast applications in optoelectronics and photovoltaics [1]. Although chemical routes are mostly used to synthesize semiconductor materials with different bandgap [2,3], yet mechanical alloying is new upcoming technology to engineer the bandgap in semiconductor nanomaterials, through both the size and composition variation [4,5]. Though mechanical alloying provides an easy route to engineer the bandgap of semiconductor nanomaterials, but has been used by very few researchers. CdPbS, CdTeSe, CdZnS, CdSe etc semiconductor materials have been synthesized by mechanical alloying [6–8]. However, the technology of mechanical alloying has still not been used to engineer the bandgap in a pristine semiconductor nanomaterial such as nanocrystalline Si (In such case high energy ball milling takes place instead of any alloying, but due to literary trend the term ‘mechanical alloying’ is used here). This gives freedom to obtain single element nanocrystalline material with different bandgaps which reduces problems associated with multi-element systems such as lattice mismatch, solubility etc.

In the present work, effect of mechanical alloying on bandgap of nanocrystalline Si powder, without addition of any alloying element, has been studied and discussed. The objective of the study was to know the variation in bandgap of the nanocrystalline Si powder as a function of milling duration.

2. Experimental

The nanocrystalline silicon powder of 5 N purity (99.999%), supplied by Hongwu International Group Ltd, China having average particle size of <20 μm was milled in argon atmosphere in an attrition mill for 4–20 h (4 h, 12 h and 20 h) to decrease the crystallite size in it. Before milling, to avoid impurities addition from mill, impeller arms and inner surface of vessel (Stainless Steel) of the attrition mill were coated with tungsten carbide (WC) using thermal spraying technique. The WC balls of 10 mm dia were used as milling media, keeping ball to powder weight ratio of 10:1. The milled powders were then degassed, to remove entrapped gases, in an oven at 200 °C in a vacuum of 10^{-2} torr for 1 h.

TECHNAI 20, FEI high-resolution transmission electron microscope (HR-TEM) was used to measure the crystallite size in the as received and ball milled powders. XRD studies was done using P’Analytical X-PERT Powder diffraction unit, using Cu Kα radiation

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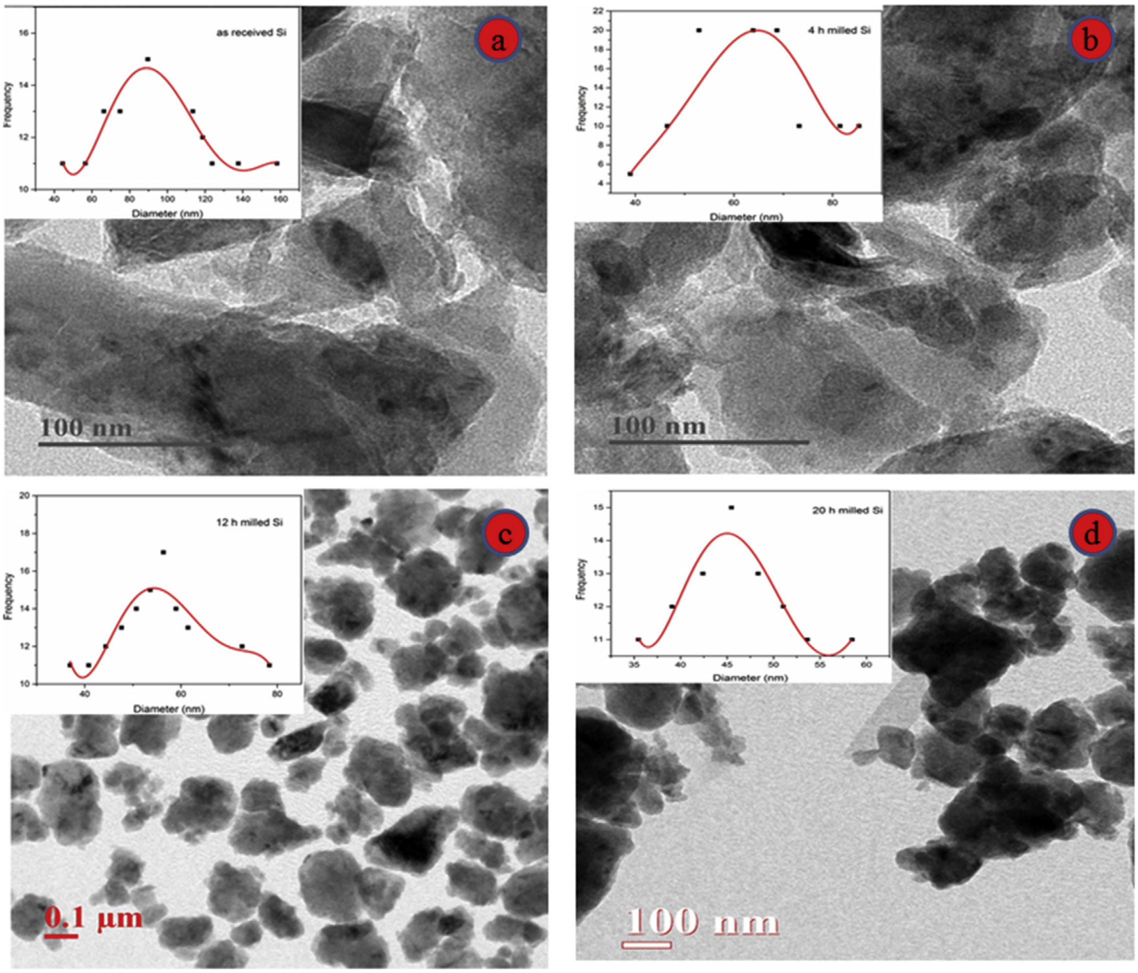

Fig. 1. Transmission electron micrographs of a) as received b) 4 h milled c) 12 h milled d) 20 h milled Si powders (inset are corresponding crystallite size distribution).

(λ = 1.5406 Å). Airix STR-500 Confocal Raman spectrophotometer, using solid-state laser (532 nm) beam of 3 mW, was utilized to determine the crystalline volume fraction in milled powders. Crystalline volume fraction is calculated from below relation:

$$X_c = (I_{510} + I_{520})/(I_{480} + I_{510} + I_{520}) \quad (1)$$

$$X_{amorphous} = 1 - Xc \quad (2)$$

where $(I_{480} + I_{510} + I_{520})$ denotes an total integrated intensity, and $(I_{510} + I_{520})$ is equal to the volume fraction of the crystalline phase. PerkinElmer Lambda 750 UV–Vis spectrophotometer was used to obtain absorption spectra of silicon powders. Tauc formula as shown in Eq. (3) [9] was used to determine bandgap from the absorption spectra of the prepared powder samples.

$$(\alpha h\vartheta)^n = A(h\vartheta - E_g) \quad (3)$$

Here, α is an absorption coefficient, Eg is bandgap and ϑ is frequency of incident is light. The value of n varies from ½ to 3 for different bandgap materials. In the case of nc-Si, due to quantum confinement, it behaves like direct bandgap semiconductor so the value of n is 2 [10].

3. Results and discussion

3.1. Crystallite size measurement

Fig. 1 shows TEM images of all the prepared powder samples. Average crystallite size was measured by TEM using ImageJ software is tabulated in Table 1 which confirms nano-crystalline silicon and reduction of crystallite size as a function of ball milling. The crystallite size distribution curves for all the prepared powders

Table 1
Crystallite size with corresponding bandgap.

S. No	Silicon powder	Crystallite size measured by TEM (nm)	Crystallite size measured by XRD (Debye- Scherrer relation) (nm)	Bandgap (eV)	Corresponding Wavelength (nm)	References
1	As received	89	91	1.25	992	[12]
2	1 h milled	88	90	1.31	946	[12]
3	2 h milled	74	84	1.37	905	[12]
4	3 h milled	71	80	1.40	885	[12]
5	4 h milled	65	69	1.47	830	–
6	12 h milled	55	64	1.57	789	–
7	20 h milled	47	59	1.62	765	–