

## Synthesis of Si Nanoparticles by Milling Technique

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### ABSTRACT

Silicon (Si) nanoparticles which studied are in the size range (7 – 23 nm) have been synthesized by mechanical milling. The milled powder was etched by HF & CH<sub>3</sub>COOH acids. The size, structural, and optical characterization of these nanoparticles were determined by X-ray diffraction(XRD), Atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and UV-VIS spectroscopy. The result confirmed that Si nanoparticles in crystal phase with band gap 3.15eV, due to the effect of quantum confinement. This technique has been shown to have an advantage over other methods of producing nanoparticles because of low cost, small particles size, low agglomeration, narrow size distributions and uniformity of crystal structure and morphology.

**Keywords:** Si Nan particles, Mechanical Milling, FTIR, Optical Band Gap.

### انتاج جسيمات السيلكون النانوية بتقنية الطحن الميكاني

#### الخلاصة

تم دراسة تحضير الجسيمات النانوية من السيلكون والتي هي بحجم يتراوح من (7 – 23 nm) بطريقة الطحن الميكانيكية. تم اظهار المسحوق المطحون بواسطة الاحماض HF & CH<sub>3</sub>COOH. و حددت الخصائص البصرية والتركيبية والحجم باستخدام حيود الاشعة السينية (XRD) و مجهر القوى الذرية (AFM) وتحويل فورييه الطيفي تحت الحمراء (FTIR) والتحليل الطيفي للاشعة المرئية وفوق البنفسجية (UV-VIS). أكدت النتيجة أن الجسيمات النانوية من السيلكون Si هي بالطور البلوري مع فجوة طاقه 3.15 eV، ويرجع ذلك إلى التأثير الحصر الكمي. وقد تبين أن هذه التقنية لديها مزايا أكثر من غيرها من أساليب انتاج الجسيمات النانوية من حيث انخفاض الكلفة وحجم الجسيمات الصغيره وانخفاض التكتل وضيق التوزيعات الحجميه وتجانس التركيب البلوري وطبيعته السطح.

## INTRODUCTION

Nanoparticles of many materials have received great attention lately, as researchers have become increasingly aware that reducing the size of materials to the nanometer scale can change their properties in fundamental ways, thus generating attractive electronic, optical, magnetic, and catalytic properties associated with their nanoscale or quantum scale dimensions [1]. Following the discovery of electrochemically etched nanoporous silicon by Canham and co-workers [2], a great deal of research has been performed on producing nanosized Si with visible photoluminescence and on characterization of its structure and optoelectronic properties [3, 4].

This luminescence from nanosized Si has been attributed to radiative recombination of carriers confined in Si nanoparticles, and its color can be modified from blue to red by changing the nanoparticles size. One benefit of exploiting the optical properties of silicon nanoparticles over other materials is the potential of silicon nanoparticles to be integrated within existing silicon technologies in order to create nanoscale optoelectronic devices. These applications include their use as chemical sensors [5], optoelectronic devices [6], solar cell [7], photo-detectors [8], and as fluorescent biomarkers [9].

Many methods have been developed for the synthesis of nanoparticles, including laser pyrolysis [10], sputtering [11], micro-emulsion [12] and chemical vapor deposition [13]. All these techniques have a common difficulty that the ultrafine particles cannot be produced in large scale. Unlike the above methods, mechanical attrition can easily produce nanocrystalline materials up to industrial quantities; mechanical attrition by ball milling has been a popular method to make nanocrystalline because of its simplicity to essentially all classes of materials [14]. In this technique starting powder particles are trapped between highly kinetic colliding balls and the inner surface of the vial, which causes repeated deformation, rewelding, and fragmentation of premixed powders resulting in the formation of fine, dispersed particles in the grain refined matrix [15].

In this work, synthesis of Si nanoparticles using ball milling technique studying and their structural and optical properties had been done. Structure and morphology properties are studied by using X-ray diffraction (XRD), and atomic force microscopy (AFM), while optical properties were studied using UV-visible absorption and Fourier transform infrared (FTIR) spectroscopy.

## EXPERIMENT

Commercially available Si- wafer was used as the starting material. The Si- wafer was milled in a mechanical milling machine at 300 rpm for two hours in a stainless steel vial under atmospheric pressure and temperature using stainless steel balls of 6 mm diameter. After milling, this powder was etched with solution of  $\text{CH}_3\text{COOH}$  and HF in water to reduce the particle size. After etching, the particles were washed with water and methanol, finally they were collected by filtration using Teflon filter. In order to study the structure of Si nanoparticles we performed that using X- ray diffract meter (Philips, PW/1710), with monochromatised  $\text{CuK}\alpha$  radiation of wavelength 0.15418 nm at 40KV and 30mA. An AFM (Advance angstrom Inc. SPM AA3000) was used to

study the particles size and morphology of milled nanoparticles NPs. A small portion of powder dispersed in DMSO (diethyl sulphoxide) and ultrasonically was used to record UV-VIS absorption spectrum.

Optical properties of the NPs were studied using UV-visible absorption, which recorded by employing a Cecile-7200 double beam UV/VIS spectrophotometer supplied by Aquarius Company for the wavelength range of 200-1100 nm. While Fourier transform infrared FTIR spectrophotometer (IR Affinity-1, SHIMADZU) was used to study surface chemical composition of NPs in the range of 400-4000  $\text{cm}^{-1}$ . KBr pellet was employed for the powder.

## RESULTS AND DISCUSSION

Figure (1) shows an x-ray pattern of prepared silicon nanoparticles, there are three main sharp peaks at  $2\theta = 28.3^\circ$ ,  $47.1^\circ$ , and  $56.1^\circ$ , which are characteristic of nanocrystalline silicon, these corresponding to the structures (111), (220) and (311), which confirms high crystalline nature respectively, while broad amorphous peak is present around  $2\theta = 20^\circ$ . The XRD data agree well with Li *et al* [16] results of the prepared Si nanoparticle by laser induced pyrolysis and Dhara *et al* [17] results of prepared Si nanoparticles by ball milling.

The chemical composition of the particles was examined using FTIR spectroscopy. An FTIR spectrum is shown in Figure (2), the broad absorption band with a peak of 3200–3500  $\text{cm}^{-1}$  and the peak at 1631.7  $\text{cm}^{-1}$  are due to stretching and deformation of OH vibrations. The peak appeared at 2862.2  $\text{cm}^{-1}$  corresponds to stretching of C–H vibrations. A broad band in the spectral area of 1350–1550  $\text{cm}^{-1}$  is due to deformation of C–H vibration. While Si–O and Si–O–Si bond stretching peaks around 459  $\text{cm}^{-1}$ , 1087.8  $\text{cm}^{-1}$  are observed. Peaks around 609.5  $\text{cm}^{-1}$  and 2335.6  $\text{cm}^{-1}$ , are due to the hydrogenated surface, related to Si–H vibration. The peak at 678.2  $\text{cm}^{-1}$  can be attributed to the Si–Si stretching mode; these results were in agreement with result in reference [17-19].

The Si–O bonds in the sample presumably come from slow air oxidization, since the particles are prepared in an oxygen-free environment and their as-prepared surfaces could consist of a mixture of H-termination and dangling bonds. While the Si–H, C–H, OH bonds were come from Washing with water and methanol as the final step in the etching procedure. Clearly, the state of the particle surface changes substantially during the etching process [17].

Figure (3) shows AFM image for Si NPs (image size 1000nm x 1000nm), figure (3b) shows the histogram of size distribution of Si nanoparticles with size ranging from (7-23 nm). While figure 4 shows absorption spectra of Si nanoparticles, the absorption is high at UV range and decrease in the visible range. Also shows there absorption peak at about 525nm shifted of absorption edge are expected due to change in nanoparticle size which is quantum confinement effect [20]. As the mean particle size decreased, it was observed that the intensity of absorption increased and also leads to widening of the band gap [21], However, the spectra are not showing the smooth curves due to the shape of the particle which are not uniform and not monodispersed. The shape of the particle also affects the shifts of the wavelength [18]. From the transmission data, nearly at the fundamental absorption edge, the values of absorption

coefficient  $\alpha$  are calculated in the region of strong absorption using the following equation [22]:

$$\alpha = \frac{1}{t} \ln \left( \frac{1}{T} \right) \quad \dots (1)$$

The energy gaps  $E_g$  of Si nanoparticles was estimated using Tauc relation [22, 23]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \dots (2)$$

Where:

$E_g$ = the band gap energy.

$\alpha$  = the absorption coefficient.

A= constant.

$h\nu$ = The photon energy.

The band gap was determined from Figure (5), the  $(\alpha h\nu)^2$  is plotted as a function of the photon energy  $h\nu$ . Silicon nanoparticles synthesized here are direct band gap semiconductors [23]. From the data plotted in figure 5 the bandgap energy is determined by using linear extrapolation. The obtained band gap energy of Si nanoparticles is  $E_g=3.15\text{eV}$  which corresponding to a blue shift of  $2.03\text{eV}$  from the band gap of  $E_0=1.12\text{ eV}$  of bulk Si due to the effect of quantum confinement. Also, the extinction coefficient  $k$  can be calculated by the following equation [22]:

$$K = \frac{\alpha \lambda}{4 \pi} \quad \dots (3)$$

Figure(6), shows the variation of extinction coefficient with wavelength, excitation coefficient related to attenuation value of electromagnetic wave where its passed through the medium, so that the high value of short wavelength related to the loss incident energy in absorption process or due to loss the wave in electron transit between the energy level but this result is reverse in long wavelength this is may be related to appear another absorption process such as absorption by charge carrier.

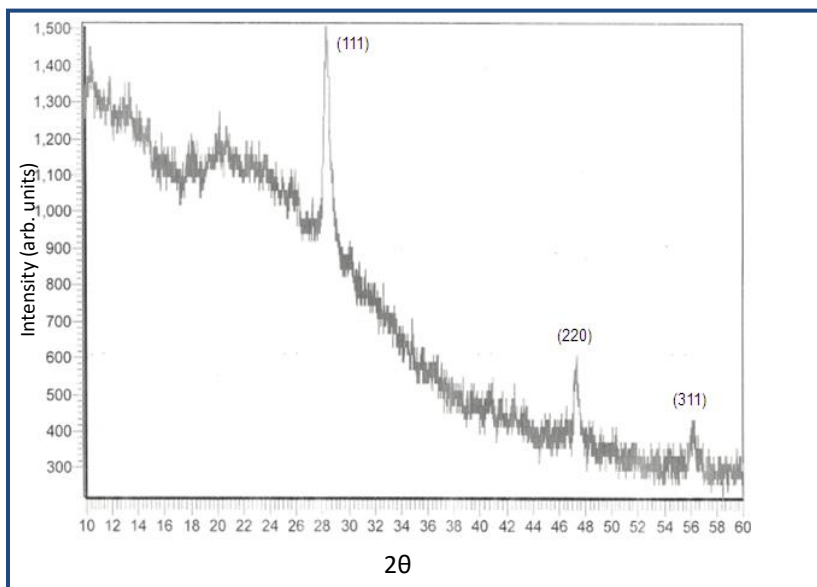
## CONCLUSIONS

Si nanoparticles have been synthesized by mechanical milling. The Si NPs were investigated using XRD, AFM, UV-visible and FTIR. X-ray diffraction patterns revealed that the Si NPs have crystal structure, with size in the range (7-23nm). The band gap energy of Si nanoparticles is  $E_g=3.15\text{eV}$ , which obtained from absorption spectra. The dispersion spectra of  $\alpha$  and also obtained from the transmission data. FTIR spectra show chemical composition of Si NPs. This technique has been shown to have advantages over other methods of producing nanoparticles in terms of low cost, small particle sizes, low agglomeration, narrow size distributions and uniformity of crystal structure and morphology.

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**Figure (1) X-ray diffraction (XRD) pattern for Si nanoparticles.**

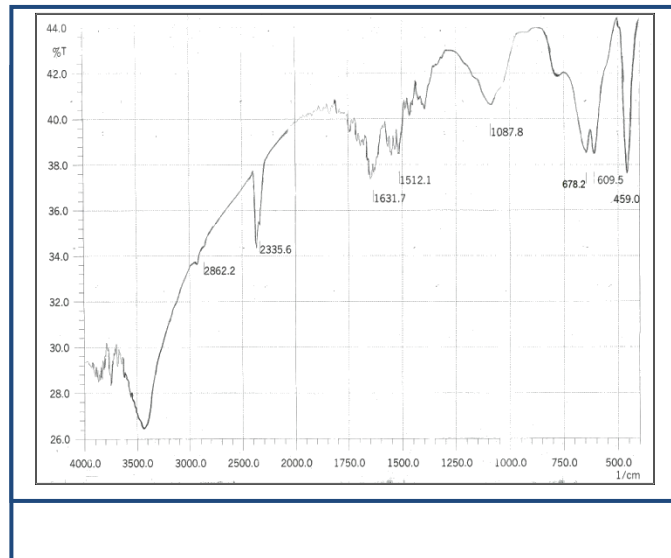


Figure (2) FTIR spectra of Si nanoparticles.

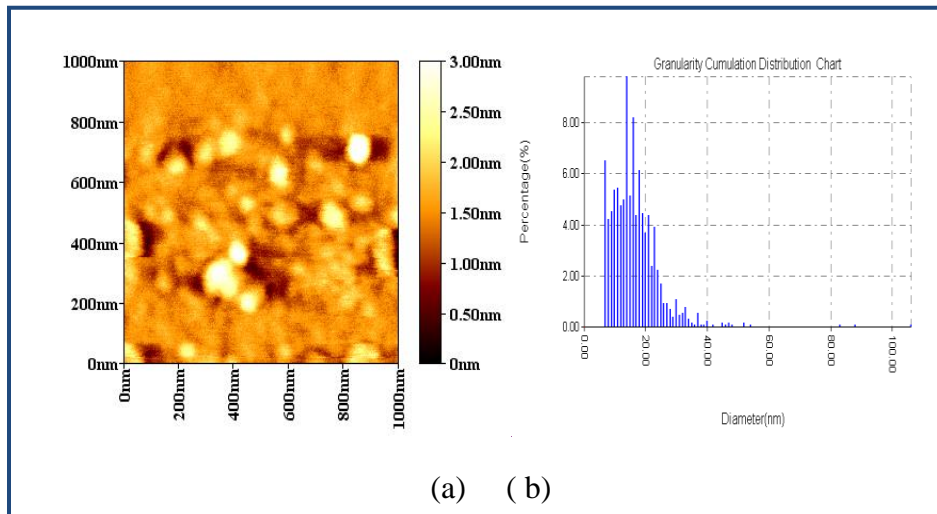


Figure (3) AFM image (1000nm x 1000nm): a) Two dimensional (2D) image for Si nanoparticles. b) Histogram of Si nanoparticles size distributions.

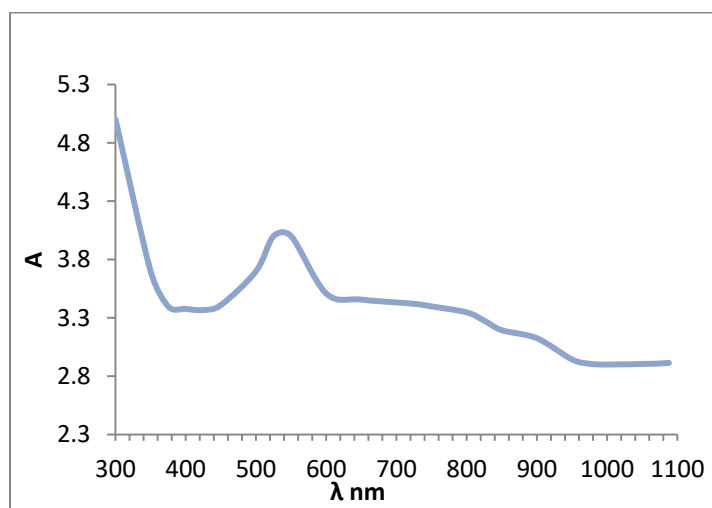


Figure (4) Absorption spectra of Si nanoparticles.

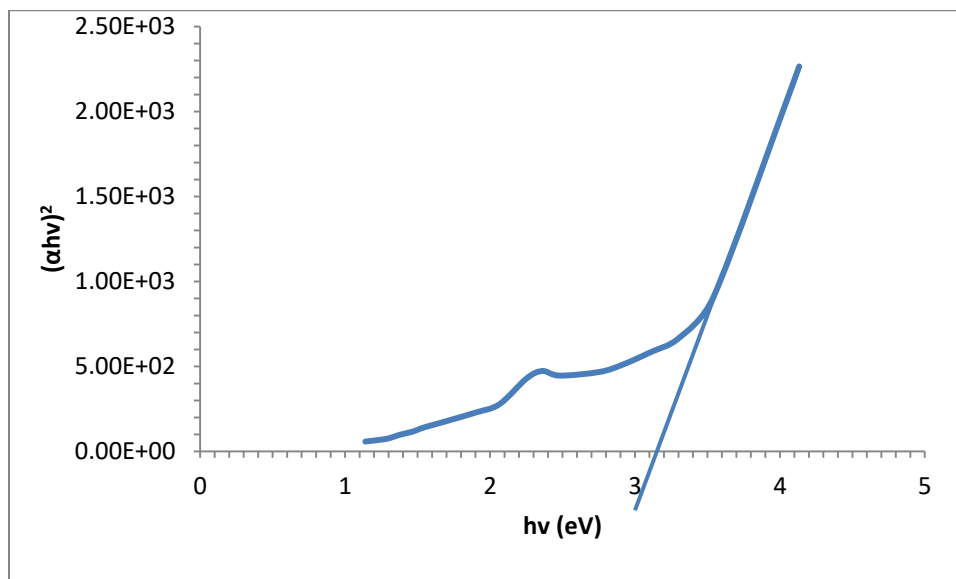
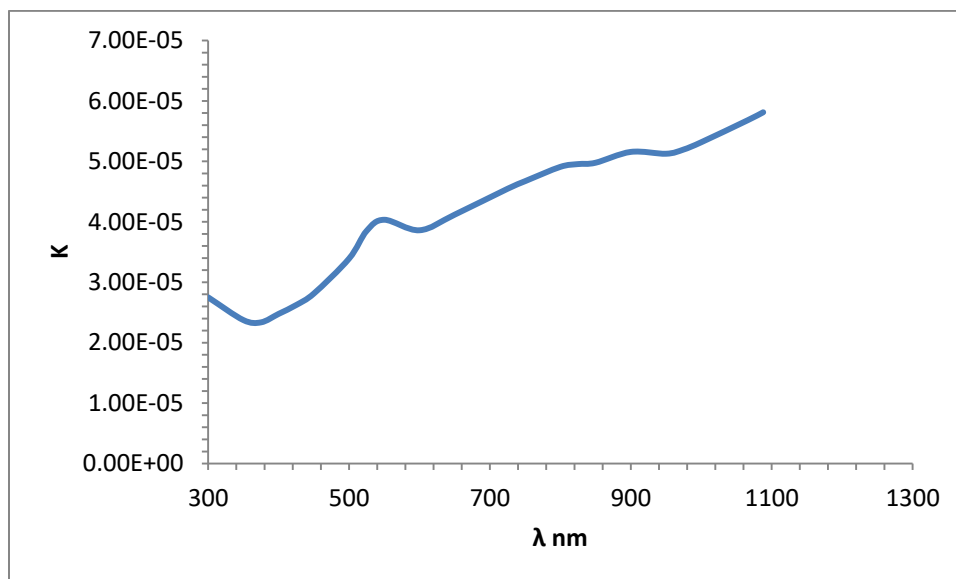


Figure (5)  $T_{auc}$  plot from the absorption spectra obtained for Si nanoparticles.





**Figure (6) Variation of extension coefficient vs. wavelength for Si nanoparticles.**