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Characterization of Germanium Nanoparticles via different methods of reaction temperature

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***Abstract*— Germanium Nano Particles have been synthesized by thermal assisted method. Through the two experiments carried out, the reaction temperature was fixes as 160 ◦ C since the beginning of experiment and in the other experiment the reaction temperature has been varied by 20 ◦C intervals from 80 ◦C and gradually increased to 160◦ C. The obtained powders have been characterized by SEM, FTIR, and XRD. It has been found that mild reaction temperatures increasing gradually leads to more Nano structures morphologies of Germanium Nanoparticles with a controlled size.**

***Index Terms*— Ge Nano particles, characterization, reaction temperature**

I. INTRODUCTION

Germanium Nanoparticles have optical and electronic properties with low toxicity. They are also suitable materials for biological and optoelectronic applications [1] .They have also been used in semiconductors and recently assembled on MWCNTs for lithium-ion batteries [2].

The main important reason of interest in Ge Nano Particles is their disparities in electronic properties from the bulk material they exhibit due to their small size. They have also been used in CNT production as catalyst [3]. They are also used in solar energy conversion [4], charge storage[5], photo detector[6].

There are some common methods to synthesize Ge Nanoparticles such as metathesis reaction, Hydride reduction of Ge Halides, Microwave assisted, sol gel and thermal decomposition of organo germane precursors. [1] In the available literature there are varieties of methods on Germanium characterization in which high pressure and temperature is used in them.[7] . There are some methods as reaction of Zintl salt with ammonium halides [8] , reduction of Ge halides by mild-strong reducing agents,[9][10] ,decomposition of GeCl4 in a plasma Reactor[11], chemical etching by HF[12]

It should be mentioned that Germanium Nano Particles preparation method and the synthesis parameters to manipulate them affects their properties for further application. [13]. There are just few reports showing the effect of reaction parameters on controlling the size of Ge.[14] . Among these methods the reduction of Germanium Halides have been proven to be efficient for controlling size and morphology [15] .As stated in the literature some parameters such as effect of precursor, precursor concentration and comparison of precursor is studied[16,17,6]. In the case of temperature there are some reports on microwave assisting [18] but not a lot for conventional and facile heating synthesis [19]

That is the reason in this work, Germanium Nano Particles have been synthesized by different methods of reaction temperatures, in one experiment just fixed reaction temperature is used and in the other experiment a gradual increase in reaction temperature has been selected in the methodology.

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II. METHODOLOGY

Methodology is a simple thermal method modification of the reports in the literature such as Dmitri and other researches [1]. It should be mentioned that there have been other methods such as laser deposition and microwave assisted method proposed and also there is a registered patent of sol gel method [19][20] and the common methods mentioned earlier in the introduction part. But since in this work the simple method was one of the objectives, the easy thermal method has been selected to use in the lab scale.

In the case of materials selection there are some reports on using Oleyamine [6, 21] and oleic acid being effective precursors to produce Germanium Nanoparticles with good crystallinity and nanostructure results [22, 23]. So because of this reason these materials are used in this research paper as well.

Knowing these facts and methods, a modified experimental method has been run to see the effect of reaction temperature on morphology and characterization of Germanium Nano Particles.

III. EXPERIMENT

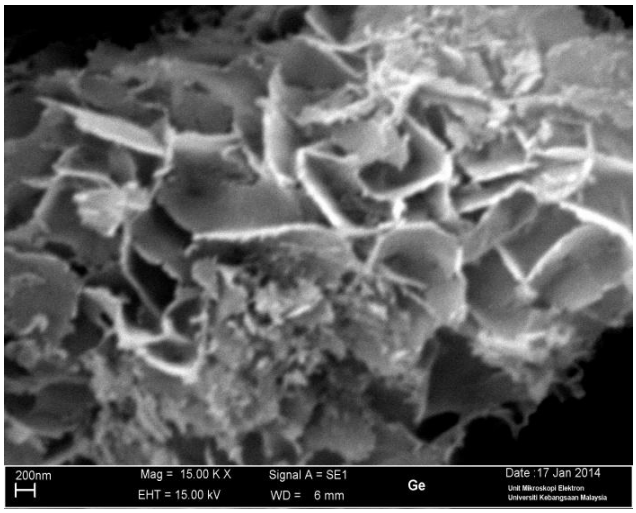
Oleic Acid, Oleyamine and methanol are combined in 20 ml beaker and mixed well on a stirrer for 4 hours , then 0.6 mmol of GeI_2 (Germanium Iodide) with molar ratio of 0.3 was added to the mixture. They were heated at a fixed 160◦ C reaction temperature since the beginning of the stirring for the first experiment and in the other run of experiment increasing reaction temperature gradually from 80 ◦ C every 1 hour for 20 degrees intervals of temperature to reach the reaction temperature gradually to 160◦ C for 4 hours, then it was observed that a yellowish solution changed to brownish which showed the reaction taking place.

Then they were transferred to oven while sealed and dried at 100 ◦C; then they were washed 3 times and centrifuged at 7000 rpm and calcined at 400 ◦C for 4 hours.

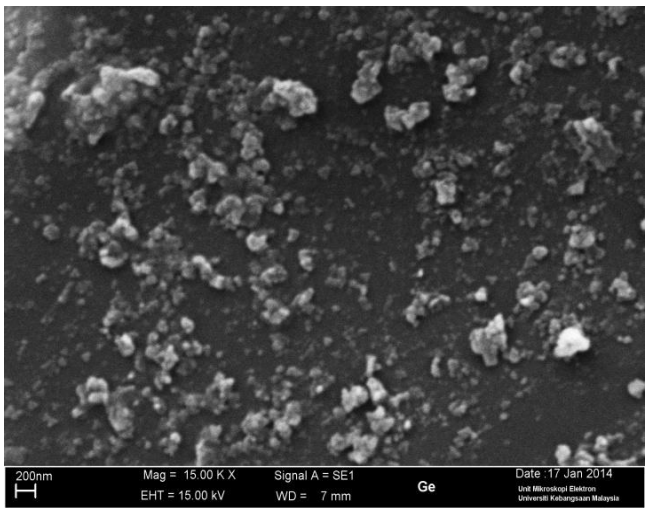
IV. CHARACTERIZATION

XRD was carried on CuK lines. They were deposited on a layer in a quartz holder and data was carried out at 2θ◦ angle and they were compared by International Center of Diffraction Data card Numbers of 04-0545 and 36-1463. FTIR and SEM were also used to characterize the obtained Nano Particles.

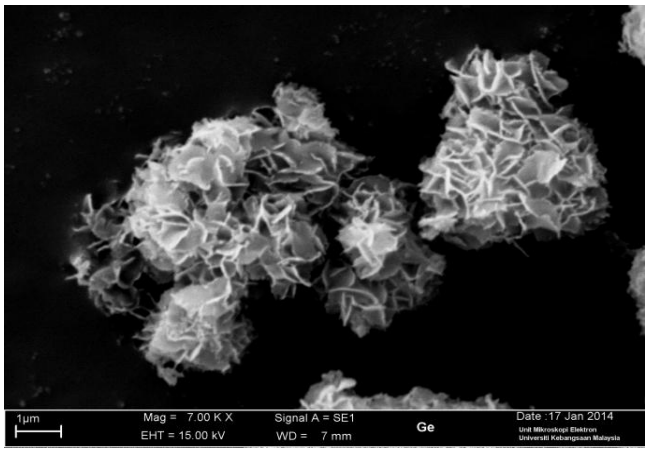
V. RESULTS AND DISCUSSION



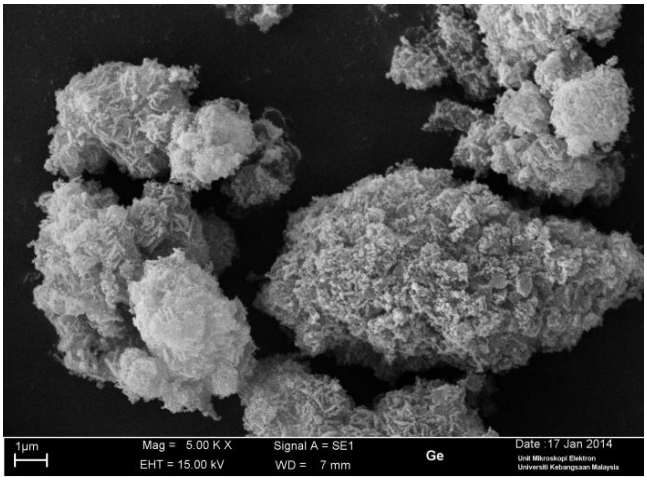
(a)



(b)

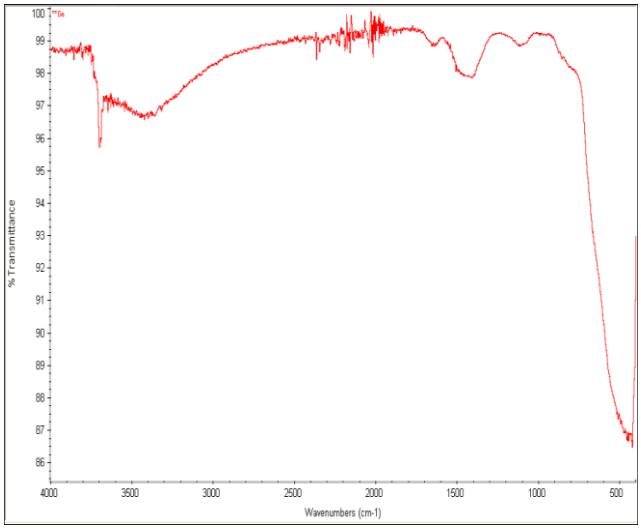


(c)

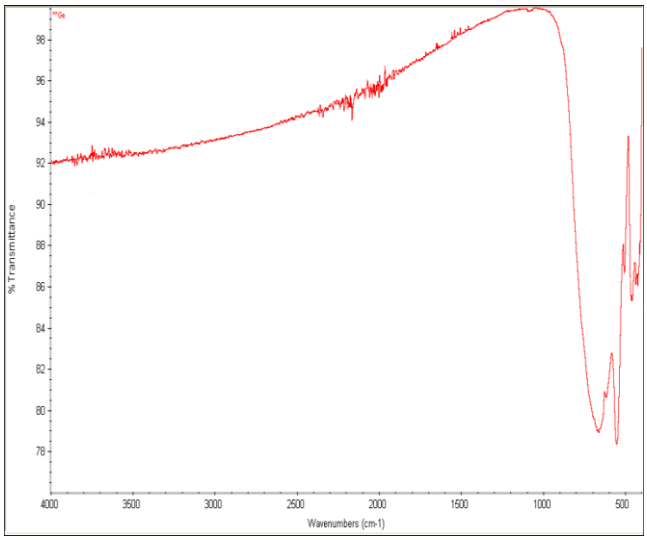


(d)

Figure 1- SEM images of Ge Nanoparticles; (a) gradual increase in temperature, (b) fixed reaction temperature, (c) gradual increase in temperature, (d) fixed reaction temperature.

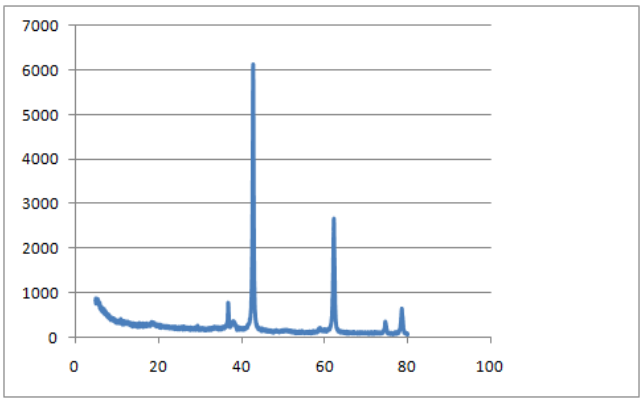


(a)

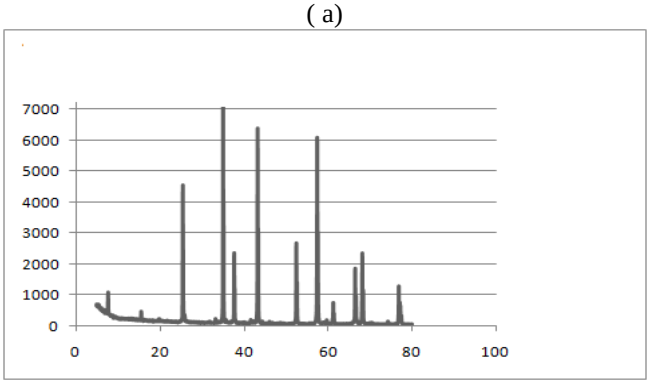


(b)

Figure 2- FTIR results for (a) Ge Nano Particles with a gradual increase in reaction temperature, (b) a fixed reaction temperature.



(a)



(b)

Figure 3- XRD patterns for Ge Nano Particles (a) gradual increase of reaction temperature (b) fixed reaction temperature.

Those Germanium Nano Particles having fixed 160 ◦C temperatures from the beginning of the synthesization have some amorphous nature, and the Germanium Nano Particles having gradual increase in temperature to 160 ◦C, crystalline. As temperature is increased the trend of being amorphous to crystalline can be seen in SEM figures. (Figure 1)
FTIR shows bands at 510, 769, 1056, and 1400. It has also measured GeO_2 and it shows Ge-OH, Ge-O-Ge peaks which are more broad stretches for the Ge Nano Particles synthesis at gradual increase of Ge Nanoparticles but more sharper for the Ge Nano Particles synthesis with the fixed 160 ◦C reaction Temperature from the beginning of the experiment. Since oxidation has occurred during measurement, $Ge0_2$ of ά type is detected. (Figure 2)

The XRD patterns peak are sharper for Ge Nanoparticles synthesized by gradual increase in temperature. Scherrer formula was used to measure crystallinity and the calculated rang of particles are 16 nm for gradual increase temperature and 23 for a fixed reaction temperature. (Figure 3)

$D = K\lambda/\beta\cos\theta$, -Scherrer formula

Where D is the crystalline size (nm),

K presents as Scherrer, which has a value of 0.89, λ is the wavelength (nm),

β is the observed peak width,

and θ is the diffraction angle.

VI. Conclusion:

As a conclusion, it was found that gradual increase in reaction temperature leads to higher crystallinity and it has also resulted in a larger difference between size of the Ge Nano particles produced by gradual and not gradual reaction temperature. Ge Nano Particles were synthesized in sizes of 16 and 23 nm for a gradual and not gradual increase in temperature respectively. It shows that more crystallinity and size control is achieved in a milder reaction temperature increased gradually.

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