Feasibility of Non-thermal Plasma Assisted Semiconductor Material Synthesis for Thermoelectric, Photovoltaic and Energy Applications

A. R. H. Rigit, M. U. Mushtaq, K. Sanaullah, A. Khan, and W. Javid

***Abstract*—Silicon being the major component in the semiconductor industry has proved itself very effective in myriad applications that include its use in transistors, energy storage, photovoltaics etc. A boom into its efficiency has emerged with the use of the Nano technology, when the same material is used at Nano scale for the fabrication of the devices in the said applications, it provides promising characteristics. Yet the synthesis techniques for the usage of the silicon as material at Nano scale encounter myriad hurdles, however, still the application of non-thermal plasma at Nano scale has found promising results in this field. It could bring about a huge improvement into its efficiency and can thus become ideal for the vast industrial uses. Yet it encounters several issues that makes this practice economically not feasible, like it needs more time to process such material rather than the conventional methods to synthesize materials on the liquid, solid or gas phases have their own short comings which will result into certain compromises the synthesizers have to deal with based on the properties of the end finished product. On the contras, Non-thermal plasma processing is found cost effective with properties like lack of agglomeration and more efficiency.**

***Index Terms*—Nano crystals, silicon, synthesizers, photovoltaics.**

I. Introduction

Silicon belongs to group IV of the periodic table with its place at the 4th group it is half way up in between the metals and halogens. 4 electrons in its valence shell makes it ideal for the use to the semi-conductor industry where the important applications of it involve the use of the silicon in energy storage devices, transistor manufacturing and photovoltaics etc. Still there is provision of the improvement into the said material it is being investigated that if the synthesis of the silicon is processed at Nano scale, it could bring about a huge improvement into its efficiency and can thus become ideal for the vast industrial uses. Yet it encounters several issues that makes this practice economically not feasible, like it needs more time to process such material rather than the conventional methods, particles may not be well distributed even with the use of the most effective modern techniques in this line and the prohibitive cost being needed for the establishment of this facility. The use of the non-thermal plasma for the synthesis of these particles is a new facet of this technology that has been introduced recently and has shown effective to address the above three short-comings to certain extent. The semiconductors group elements have the tendency to tune the property in them to address the targeted properties needed in them for the issues like surface coating of desired properties. Such a property can be achieved using desired discernibility into the solvent to achieve the desired end. Non-Thermal Plasma can change the chemistry of the surface by bringing the changes into the gas phase of the solvent. A visible advantage of this process can be seen in using the group IV elements coatings on the anode in the batteries to improve its stability.

II. Nano Materials Characteristics

Nano materials offer a very promising side of properties due to their inherent ability to be dispersed uniformly, thus establishing the uniform core of properties across all the material body. During the last decade several improves in this regard are the clear proof of this very fact that this technology has proved its effectiveness on every front [1], [2]. The usage of the semi-conductor materials synthesized and fabricated using Nano technology has not merely confined to semi-conductor applications, rather it ranges its usage in biotechnology, military applications, energy production, storage, environmental technologies and in medical applications. Being lying between the very small i.e. atomic scale and very large i.e. macro scale, Nano materials can change the properties of the same material to considerable extent. Most of the properties that include mechanical, electrical, optical and thermal can be improved if the material is synthesized and processed from bulk to Nano scale. The main change that has been brought into the properties of the material is due to the changes in the energy level and band gap, where any change into these two parameters bring change into the properties of the material that are dependent on size. Yet all the elements from group 2 till group 6 have been used in myriad technologies including the photovoltaics, light emitting diodes etc. [3]. But group 4 elements have less

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energy levels and band gaps than the rest of the elements of group 2 till 6, which make these elements most suitable for the purpose.

III. Effect of Size on the Semi-conductors Properties

Group 4 elements of periodic table show different properties which are mainly dependent on their structures, bonding with chlorine and hydrides and oxidation states, which bring the variation within the same group from metals to non-metals. Whereas with in the same group based on the allotropic properties Tin is available in semi-conductor as well as conductor [4], [5]. Due to the strong covalent bonds in carbon it has high boiling and melting points [6]. In addition to it silicon has the most prominent place in this group with myriad applications in technological industries whereas it composes 28% of the whole earth crust [7]. Silicon shows both metallic and non-metallic properties when it's size is reduced to 4nm. Its optical and electrical properties have been changed a lot due to surface effects. For example, the photoluminescence intensity can be adjusted with the help of the variation in the band gap and particle size. Several efforts have been made to address the issue of the particle size using size controlling methods [9], [10]. The reduction in photoluminescence intensity due to the removal of hydrogen has resulted into the blue shift which is still a problem being prevailed [8], [9]. At different particle sizes the peak energy for silicon has different values [10] as shown in Fig. 1, where the size distribution effects the photoluminescence properties of the materials [11], [12], the presence of oxygen and nitrogen also affects the properties of the materials to a large extent [13], [14]. Since the effect of the size is directly associated to the band gap, the band shift is thus directly correlated with the particle sizes [15]. Literature shows that the silicon has the prominent optical properties out of all the elements in the group 4 [16], [17]. The dispersion of the Nano particles inside the material matrix results into the formation of the material suitable for the LEDs or photovoltaic applications [18]-[22], where the Nano crystals are the building blocks of the transistors that have prospective applications in thermoelectric, electronic, photovoltaic and batteries [23]-[28].

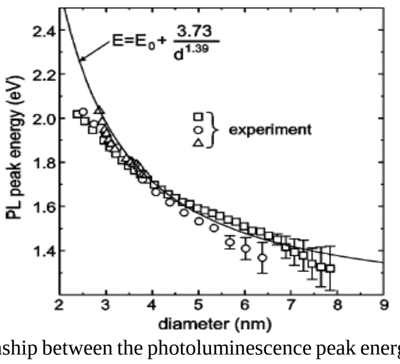

Fig. 1. Relationship between the photoluminescence peak energy and particle diameter [10].

IV. Conventional Synthesis Techniques

The synthesis techniques of the Nano silicon are based on the phases in which it has been synthesized. When chemical reactions take place in solvents this gives birth to the methods such as evaporation, decomposition, sol gel, and precipitation. Most of the Nano-particles belong to the elements of group 2 till 6, which have been synthesized using chemical methods, but these produce wide distribution of the particles with the low quality Nano particles, so such methods are not preferred for silicon synthesis. The reason is being the elevated temperature and pressure environment that is needed for the formation of organosilane [29].

Milling is another method that can produce Nano particles as small as 5nm [29]. Gas phase techniques are useful to produce high quality Nano particles. Pulsed laser technique is another technique which can be used for the purpose where the target is a small piece of metal and laser is pulsed at femtosecond's rate, which ejects the silicon atoms out from the surface and thus forms the Nano particles with less contamination from the surface. Here, gases like argon helium etc. have been used for the treatment of the surfaces using the laser impingement. The pressure of these gases has also effect on the nature of the particles as investigated by the use of the fluid inertial model. It has been found that if the pressure of the gas has been raised, it will help in increasing the particles size and binding energy between them [30], as shown in the Fig. 2.

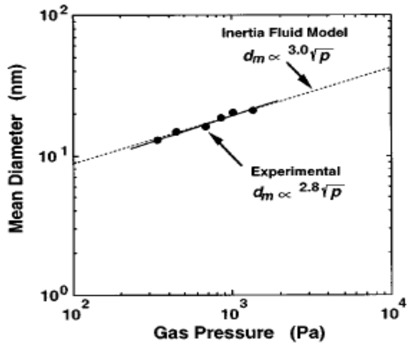

Fig. 2. Relationship between particle mean diameter and ambient gas pressure [30].

V. Non-thermal Plasma Synthesis of Nano Particles

Nano particle synthesis can be conducted in three different methods that include liquid, solid and gas but each of these methods have their own draw backs. It includes:

Liquid Phase: High cost, long processing time, multiple steps involved, and large amount of solvents used.

Solid Phase: Controlling the shape and size of the nanoparticles.

Gas Phase: Require high temperatures which yield size distribution because of particle agglomeration.

Plasma is another method used for the synthesis of the Nano-particles, whereas the main advantage of using the plasma is the thin film of silicon that can be deposited on another material for the sack of modified surface properties using the deposited surface. This technique needs no high pressure or temperature, so it's cost effective. As plasma is composed of 4th state of matter so it contains itself high energy electrons and other entities [31], which can be used for the purpose of synthesis. The electric field is applied across the material with the inert gas as medium between the material and the electrodes. The temperature of the gas species reaches to about 200, 000 K to 50,000 K before the material has been bombarded to produce the Nano particles whereas the radii of the produced particles depends on the temperature of the electrons [32]. The generation of the negative particles inside the NTP is advantageous in the sense that it depreciates the agglomeration of the Nano sized particles. Since the polymers show both conductive as well as metallic properties therefore, the use of the polymers seems favorite for being used in the electronic applications till medical sciences. Also, the reflection of light from the Silicon based Nano structures has been observed that sparks the application of this phenomena in illuminations using solid state lightening, optoelectronics and fluorescent agents for biological applications. The innovation still lacks control on production of desired results so different approaches have been adopted to attain the optimum high yield synthesis process for the desired purpose [13]. The improvements that have been brought about in this regard include surface functionalization of Silicon and Germanium Nano crystals for their application in the fields of photovoltaics and luminescent [33] along with efforts to address issues related to identification of microstructure, surface chemistry, mono-dispersity and doping [34]. On germanium side the effort to control the size of the nanocrystal results into promising achievement as it has been found that the size can be controlled via modifications in the residence time of the crystals within the plasma environment [35]. Similar efforts can be found elsewhere in literature for Si [36] as well as for sub-10nm, core shell, and carbon-coated crystalline Si (c-Si) Nano particles for energy related applications [37]. Around 3-15nm sized crystals have been synthesized at H_2 concentration of around 5-70% and pressure of 1-12 Torr with major dependence of the size is being on the residence time [38]. The use of the FTIR spectroscopy and thermal effusion have been made to synthesize 3-5 nm particles of crystalline and amorphous Silicon (Si). It has been found that at higher power of plasma Si particles have been crystalized in gas phase [39].

Plasma synthesized in-situ organic functionalization of hydrogen terminated silicon Nano crystals have been performed using total reflection FTIR spectroscopy. It has been observed that while doing hydrosilylation of Si Nano crystals the paths of alkenes and alkynes are different, which have proved useful in surface ligand passivation [40]. Some reviews papers and thesis on research findings related to non-thermal plasma synthesis of Si Nano crystals for photovoltaic, solar and other related applications are very useful in this regard [41]-[45].

VI. Plasma Polymerization

The formation of a polymer layer under the condition prevailed inside the Non-thermal plasma reactor is called Plasma Polymerization. There are two types of reactors used for the purpose, one is bell Jar and the other is tubular type reactors. In bell jar two parallel plates have been excited using the DC current whereas in the case of the tubular reactor, Radio Frequency (RF) source is coupled with the power source [46]. The properties of the material thus produced are related to the conditions prevailed inside the reactor [47], whereas the distance between electrodes, electrode sizes and power are the three parameters which are the determining factors for the particle sizes as compared to the power and the flow rate [48], [49]. The main advantage of using the Non-thermal plasma source is the reduction in the processing time which has been achieved using plasma processing of the materials for Nano particle synthesis and thus producing materials with enhanced properties.

VII. Conclusion

Materials show enhanced properties when their particle sizes change from bulk to Nano scale. Nano scale material synthesis provides added advantage due to the uniform size distribution as well as better surface properties due to lower energy gap and band gaps. To synthesize materials on the liquid, solid or gas phases have their own short comings which will result into certain compromises the synthesizers have to deal with based on the properties of the end finished product. On the contras, Non-thermal plasma processing is found cost effective with properties like lack of agglomeration and more efficiency. Further improvements can be brought into the processed material if provided with the more conductive Nano particles layer in the plasma polymer and further investigations can be conducted on the issues of the mechanical stability of the added layer. These studies could help to find the ways through which stresses can be reduced inside the material being used as coatings on the electrodes in the batteries.

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