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Prospects of Microwave Heating in Silicon Solar Cell Fabrication – A Review

S. D. Das
CEGESS, Bengal Engineering and Science University, India

Abstract : *Solar energy is only renewable energy source that does not depend on earth's resources. Current industrial manufacturing of solar cells use manufacturing steps that have many sustainable issues. So it becomes very important to promote technologies that are more sustainable than current state of the art. This paper will look into prospects of microwave heating for silicon solar cell fabrication in this perspective. Microwave heating is very different from conventional heating techniques and application of microwave for semiconductor processing purposes has many advantages. It provides avenue to crystallisation of amorphous solids, reduction of defects, selective heating, reduction in processing time, sintering of powdered materials and so on. Sustainability analysis of microwave heating over conventional heating will be presented to judge its suitability in solar cell fabrication. Status of different technologies using microwave heating which could replace or assist in different fabrication steps of solar cells will be reviewed. Based on these reviews, possible fabrication schemes of silicon solar cells will be presented.*
Keywords *- microwave heating, solar cells, silicon, nanomaterials, sustainability*

I. Introduction

Microwave radiation is part of electromagnetic spectrum with frequencies ranging from 300 MHz to 300 GHz (Fig. 1). Dielectric heating is heating of material using high frequency electromagnetic radiation and microwave heating is subcategory of dielectric heating at frequencies above 300 MHz. Use of frequency in the RF range (1-300 MHz) for heating purpose is not uncommon. This process of heating with electromagnetic radiation is also known as electromagnetic induction heating [1]. Most often materials are heated with in a cavity where electromagnetic waves are launched from a small dimension source such as a magnetron. These are referred to as microwave ovens. The first commercial microwave oven was available as early as 1947 from Raytheon. Microwave oven finds its most popular use in domestic application for heating of food materials. There are many industrial applications of microwave heating as well, such as melting, smelting, sintering, drying, joining, annealing [2-13] and many more. Some of the applications rely on indirect heating through susceptors [14]. Microwave heating without the use of cavity is also possible and one such example is asphalt pavement maintenance, where a heating wall is used instead of a cavity [15]. Microwave heating could be adopted for semiconductor processing as well. Microwave annealing in semiconductor processing is a potential alternative to conventional rapid thermal annealing (RTP). Microwave annealing can deliver much higher power in less time than RTP (Fig. 2) [16, 17] and this can lead to extraordinarily high ramping rates of >2000 ^{o}C/second in some materials [18]. There are many other applications of microwave heating in semiconductor processes such as non-contact heating and selective heating, defect elimination in semiconductors, ultra fast annealing, and recrystallization of amorphous semiconductors [19]. Solar cells based on microwave heating have recently been introduced by Herman et. al. [20], where microwave heating has been used to produce nano-particles and thin film solar cells were then produced using microwave annealing procedure. In this review an attempt is made to discuss possible applications of microwave heating for different fabrication steps of silicon solar cells. Discussion on sustainability issues of microwave heating will also be presented to justify its suitability in solar cell fabrication. Also, part of the discussion will focus on nanomaterial fabrication using microwave heating, which could be used for novel third generation solar cell designs such as plasmonic based solar cells. Based on the reviews, technically feasible fabrication schemes of silicon solar cells will be presented.

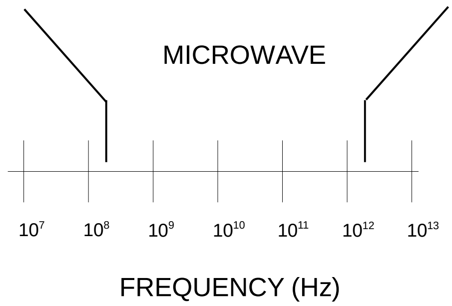

Figure 1. Electromagnetic spectrum showing microwave range.

II. Microwave Heating

Microwave heating is very different from conventional heating. In conventional heating, thermal energy is transferred into bulk of material from a heat source though conduction or convection via surface of the material to be heated. However, in microwave heating microwave radiation generates heat in the material bulk causing temperature to rise inside the material and subsequently thermal energy travels outside via the material surface. Thus conventional heating relies on heat transfer where as microwave heating relies on heat generation in the bulk, which could cause rapid rise of temperature in the material. With the rapid increase in temperature materials could soften and subsequently could melt. Once radiation is stopped cooling begins. During microwave heating some parts of sample may be heated to higher temperatures as compared to other parts of the material, this is selective heating. Selective heating happens primarily because of spatial distribution or anisotropy of material property such as dielectric function.

There are various physical mechanisms of microwave heating. Mechanisms of microwave heating could be classified broadly into two different categories, dielectric polarization [16, 21] and ionic conduction [6]. Polarization mechanisms depends on the creation of dipoles or permanent dipoles already present in a material. On application of electromagnetic radiation the fields exert force on the dipoles on atomic scale. Since the fields oscillates the dipoles have to oscillate with them. But atomic and molecular bonds of the material oppose this oscillating force, which creates intermolecular friction and the dipole is unable to keep up with the phase changes of the fields. This frictional loss generates heat. Polarization mechanisms include electronic polarization, atomic polarization, dipolar polarization and space charge polarization. Electronic polarizations is polarization due to displacement of nucleus with an atom. Atomic core is too heavy to respond to the oscillations. Only the surrounding negative charge of electrons tend to oscillate. Electronic polarization occurs at very high frequencies, near ultra violet range. Atomic polarization is polarization due to displacement of an atom with in a molecule. Only infrared frequencies can excite this mode. Dipolar polarization is polarization due to permanent dipoles present in a molecule. Millimeter and centimeter frequencies can excite this mode and this is the fundamental mechanism that governs the microwave dielectric heating. Space charge polarization is polarization due to presence of free charges. The free charges (free electrons) on encountering some boundary (such as interface between two materials) creates local electrically polarized region. Dielectric heating is negligible for electronic and atomic polarizations as time scale is too long at microwave frequencies. The other mechanism of microwave heating is ionic conduction which generates heat due to drift of charge carriers in presence of electric field against electrical resistance. Dominating mechanisms of heating inside a material is thus dependent on material and frequency of operation. The most common frequencies in use lie in Industrial, Scientific and Medical frequency band out of which use of 2.45 GHz is most common. However, other frequencies such as 0.915 GHz and frequencies in the range of 0.9 to 18 GHz are also in use for microwave heating purposes [22]. For semiconductor materials with low complex dielectric constant, the absorption of microwave energy is low while with high complex dielectric constant absorption of microwave energy is high. In case of highly conductive materials such as metals, microwave energy is only absorbed within a skin depth from surface and rest of the energy is reflected from the surface. For this later case, eddy current is the significant cause of heating [19]. In highly doped semiconductors selective heating could be achieved with microwave heating where microwave will only heat the highly doped regions. In 2009, Tian et. al. have shown specific layers could be targeted for heating in semiconductor hetero-structures with high and low doping layers using microwave heating [23].

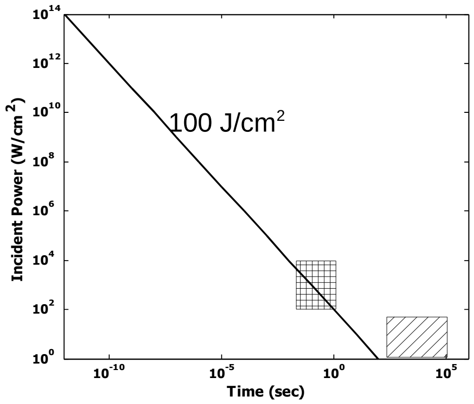

Figure 2. Comparison of microwave annealing and conventional rapid thermal annealing [16].

III. Microwave Heating Sustainability

One of the main advantage of microwave heating is that it is more sustainable than conventional heating. Sustainable development can be defined as a social development which fulfills the needs of present generation without endangering the possibilities of fulfillment of the needs of future generation [24]. From this definition a technology should be sustainable when it is economically viable, socially acceptable and ecologically viable for long run. Microwave oven which can raise temperatures up to thousand or couple of thousand degree Celsius is cheaper than conventional furnace systems as system requirements such as insulation, ceramic/ quartz tubes and other expensive parts are not required. Also, microwave heating is much more efficient than conventional furnace as heating is directly produced inside the material which prevents loss of energy due to heating of ambient. In conventional furnace there is significant loss of energy due to heating of ambient and extra insulation material may be required to achieve high temperatures, which increases the cost of the conventional furnace system. From the perspective of ecological systems sustainable technology should use renewable resources, processes should be efficient and emissions or disposed materials from the technology should not harm the ecology in anyway. Interpretation of these boundary condition for different technologies will be different for different places. Thus sustainability of a technology is evaluated with respect to its local environment [25].

Fig. 3 demonstrates the interaction of ecosphere and technosphere for microwave heating process, in general. Conventional heating system and microwave heating system differs in their process of conversion of electricity to heat and corresponding instrumentation. Definitions of renewable and non-renewable resources can be adopted from Dewulf et. al. work [26]. Microwave oven consist of four parts, namely, the source (magnetron), transmission waveguide, applicator and the electronic control unit for source and applicator. The magnetron source, applicator and transmission waveguide all are primarily made of metal while controlling unit consists of electronic grade semiconductor materials. These materials can readily be recycled. However, some microwave ovens may use ceramic insulators like beryllium oxide which may be harmful to health. Other sources of non-renewable materials are paints, wiring insulation, and non-degradable plastics. The single cycle gaseous waste depends upon the material being heated and long term wastes harmful to ecology are the non-renewable materials. However, some of these same non-renewable materials may also be used in conventional furnace along with more harmful materials such as glass wool (as insulator) in some systems, which are also hazardous to health. Thus microwave oven is more sustainable than conventional furnace system by virtue of cost benefits, being more efficient and less non-renewable material use. Further, microwave processing itself is expected to achieve good combination with distributed renewable energy such as solar cell, wind energy and small hydro systems as microwave processing could be typically characterized by short time, small scale and distributed type processes [27].

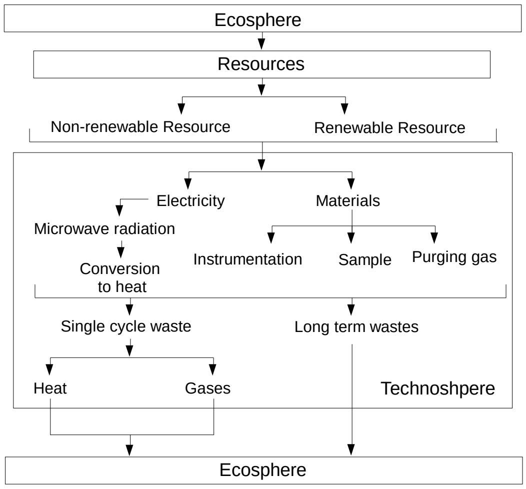

Figure 3. Interaction of ecosphere and technosphere of microwave heating process.

IV. Microwave Heating in Silicon Solar Cell Fabrication

Crystalline silicon solar cells are most widely used commercially available solar cell whose market share is largest among all forms of solar cells. A crystalline silicon solar cell is basically a p-n junction diode operated in the 4th quadrant so that power could be extracted from it. Commercially available cells typically have n on p configuration where n-region is known as emitter and p-region is known as base. A simple schematic of silicon solar cell is shown in the Fig. 4. Commercial crystalline silicon solar cells are manufactured using five basic processing steps:

1. Saw damage removal and texturing
2. p-n Junction formation
3. Anti-reflection coating and surface passivisation
4. Electrical contact formation and annealing of contacts
5. Edge Isolation

After production of solar cells, solar panels are made according to wattage requirement of the applications.

4.1 p-n Junction formation

The emitter region is formed by doping a p-type silicon wafer with n-type impurity in n on p configuration. A saw damaged removed and textured p-type silicon wafer is doped with n-type dopant using diffusion process in diffusion furnace/ LPCVD system. This process is followed by phosphorous glass removal (when phosphorous is used as n-type dopant and $POCl_3$ is used as source of phosphorous) which completes the p-n junction formation process. Two different types of emitter doping profile, deep emitter and moderately doped or a shallow emitter with high surface concentration could be used. Both these profiles with good quality surface passivization can lead to reduced surface recombination and hence increased emitter collection efficiency [28]. However, to get good quality ohmic contacts heavily doped emitter regions and base regions are a requirement. Thus the standard solar cell configuration becomes n+ – p – p+ . The heavily doped emitter and base (n+ & p+) regions can cause recombination losses and hence needs to be minimized. The front contact recombination losses due to heavily doped emitter region is minimized by keeping the emitter thickness thinner than the diffusion length of minority carrier, while a built-in electric field is created at the back surface of the solar cell or the base. The back surface field helps in minority carrier transport helping the largest number of minority carriers cross the junction quickly so that recombination losses are kept at minimum. In this case only recombination losses at front outer surface accounts for loss of photogenerated and injected minority carriers. These recombination losses are severe for wavelengths less than 500 nm as heavily doped silicon's absorption coefficient is very high at these wavelengths. If the doping emitter profile is deep and surface recombination is high, the open-circuit voltage (V_{oc}) and short circuit current density (J_{sc}) are both affected severely [29], which intern affects the solar cell efficiency. Very shallow junctions (~100 nm) with high doping densities ~10^{20} cm^{-3} are very difficult to make using diffusion methods because conventional annealing steps that follows causes emitter profile to change due to stimulation of defect formation which intern causes lateral diffusion of dopants [30]. For ion implantation method high temperature annealing step is absolutely necessary for the removal of damages and activation of dopants. But with high temperature annealing, diffusion of dopants is still a concern [31]. Quality of junction determines the efficiency of a solar cell and quality of junction depends on the dopant, dopant source, doping and annealing techniques. Typical industry standard $POCl_3$ junctions are of 300-600 nm deep and have 1-3□10^{20} cm^{-3} surface dopant levels. Rohtagi et. al. [32] have reported 19% cell efficiency with phosphorous implanted and diffused emitters.

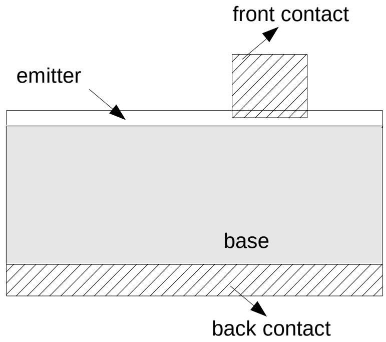

Figure 4. Simple diagram of a common monocrystalline silicon solar cell.

Junction formation can also be carried out using microwave heating by recrystallization of ion implanted amorphous silicon. Microwave recrystallization of amorphous silicon can be done with and without the use of susceptors. Vemuri et. al. [33] have recently shown that 40 seconds of susceptor assisted microwave annealing can completely recrystallize amorphous silicon doped with ion implantation technique with 1300 W – magnetron and 2.45 GHz frequency. The complete recrystallization was supported by Raman Spectra results which showed peak at ~520 cm^{-1} for all annealing times greater than 40 seconds. Complete activation of dopants was also shown with increase in annealing time. Lowest sheet resistivity of 81 Ω/sq. was obtained for 180 keV, 1×10^5 As^+ cm^{-2} and 100s annealing time. Further, diffusion for arsenic dopants have been shown to be less than conventional RTA. However, a band of defect is observed where the amorphous to crystalline interface lies with in the as-implanted structure. This was attributed to migration and precipitation of vacancies at interface. A similar study was done by Thomson et. al. [1], with single mode microwave oven which was operated at 3000W at 2.45 GHz . The dopant species in this case was boron (p-type for silicon). The higher power requirement is due to non susceptor assisted annealing. The results showed sheet resistance < 300 Ω/sq is achievable. A low ~6.5 nm shift in emitter profile was observed due to diffusion of boron. Lower value of implanted boron sheet resistance (>100 Ω/sq) with annealing time of 600s is possible and this was shown by Alford et. al. [34]. Alford et. al. achieved these results for susceptor assisted case and attributed the low activation of boron to lattice damage and reverse activation. Fong et. al. [35] achieved 81% crystallization of as-deposited amorphous silicon of 40 nm thick (without implantation) on glass substrate at a temperature of 550 ^{o}C with 1000W elliptical applicator (2.45 GHz). This result was obtained using SiC susceptor and for annealing time of 600s. The grain size of the resulted poly-crystalline structure was ~200 nm. It was observed better crystallization could be obtained with higher microwave power and higher temperature of annealing. A comprehensive study on junction formation was carried out by J Borland et. al. [36] in 2011 with implanted phosphorous and boron in silicon and under various annealing condition and techniques. Simulated results of this study showed greater than 20% efficiency is achievable using peak doping concentration of $\sim 1\times 10^{19}$ cm^{-3} and with junction depth of 400 – 900 nm (Fig. 5). In deeper junctions surface activation level is limited by dopant concentration due to increase in surface lifetimes which could result in 100% dopant activation. Thus deeper junctions would be preferable for higher solar cell efficiency [37]. Experimental results showed 5 minutes microwave annealing can achieve lower sheet resistance values (< 100 Ω/sq.) as compared to higher temperature 750 ^{o}C (90min) and 850 ^{o}C (60min) with conventional furnace anneals at the greater than 1×10^{15} cm^{-2} phosphorous implant doses and at as-implanted junction depths of 200 – 300 nm. For this study microwave annealing at 500 ^{o}C was carried out. Boron activation concerns using microwave annealing have also been highlighted in this study. M-H Tsai et. al. [38] have proposed two step microwave annealing method for activation of implanted boron. However, this method only yielded 436 Ω/ sq.

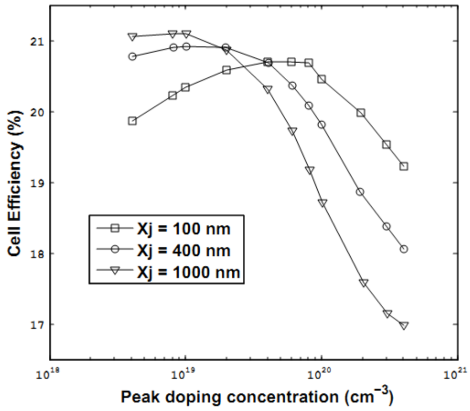

Figure 5. Solar cell efficiency as a function of emitter peak doping level for different junction depths (simulated results adopted from J Borland et. al. [36] work).

Amorphous silicon (a-Si) can be deposited with various PECVD and sputtering techniques [39 - 43]. A Brighet et. al. [44] has reported 1 μm thick a-Si film while T. Karabacak et. al. [45] have reported high growth rates of 10.7±0.5 nm/min of such deposition with different techniques. Thus amorphous silicon film thickness up to 1μm can be deposited for microwave solar cell applications. Also a-Si can be doped as n-type and p-type according to need [46, 47].

Advancement of microwave heating in junction formation is not limited to shallow junction formation only. P. Livshits et. al. [48, 49] have introduced a new method of local doping using microwave heating called point-contact microwave technique. A point contact microwave applicator is shown in the Fig. 6. In this technique, a hot spot is created below the point contact of the electrode due to concentration of near-field microwaves. This rapid heating causes the material of the point contact to diffuse into the wafer. This phenomenon is confined to the hot-spot region only. Thus this type of local doping can be designed for selective doping. Microwave input power has almost liner relationship with junction depth. P. Livshits et. al. have successfully doped silicon wafer with silver and aluminum dopants. Results of silver doped I-V (current-voltage) characteristics shows slight slower turn-on as compared to commercial p-n junctions. The difference in current at forward 1V is less than 20 mA. Further the doping region was kept below 1 mm in lateral direction. Thus this technique can be explored of selective emitter doping technique. Selective emitter doping improves efficiency of a cell by improving upon low wavelength absorption of the cell.

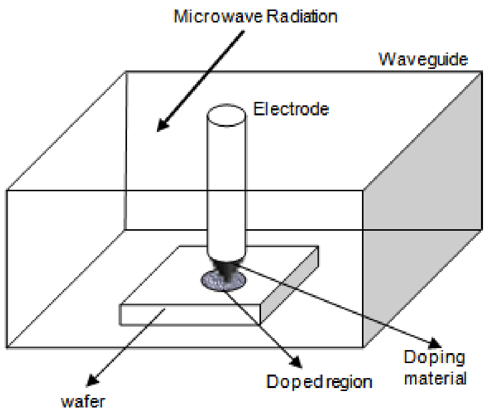

Figure 6. Schematic of point contact microwave applicator.

4.2 Anti-reflection Coating

Junction formation is followed by silicon nitride (SiN_x: H) deposition with up to 40% of hydrogen [50]. This layer acts as anti-reflection layer [51] and provides good surface passivation as well [52]. Very little work has been carried out on microwave annealing of PECVD deposited silicon nitride. Si_3N_4 is a poor absorber of microwave energy up to a critical temperature. This is because the conductivity of silver nitride is very low (~10^{-16} S/cm [53]) and as skin depth of a dielectric material is proportional to square-root of conductivity [54], at 2.45 GHz skin depth would of >1000 cm. Above critical temperature dielectric loss increases and hence could start to absorb microwave energy [55]. Typical thickness of silver nitride on silicon solar cells is ~65 – 70 nm. Thus most of the microwave energy would pass through the silicon nitride layer.

4.3 Electrical contact Formation

Most popular commercial technique for electrical contact formation is screen printing [56]. Other techniques such as buried contacts have also been commercially used [57, 58]. In screen printed method standard H-grid patterns are printed using silver paste on front side of the solar cell and the back contact is formed using two similar steps in which first Al/Ag rear busbars are printed and then in another step Al is printed to the rear of the solar cells. Each of these steps are followed by a drying step. Contact annealing or contact firing step is carried out to burnout the organics, form percolating network of silver particles and to create sintered metal films on both front and rear. Sintering reduces the contact resistance and metal film resistances. This intern reduces the series resistance of the cell and increase the cell efficiency. However, an optimum design of the front contact is required such that both shadow loss and series resistance should be optimally minimum values such that efficiency of the cell is maximized. Shadow loss is dependent on front contact area coverage and metal film resistance is dependent on film thickness and film resistivity. Typical metal finger in H-grid design is ~130μm ×12μm (single printing) with specific line resistance ~3μΩ-cm^2 and typical contact resistance ~1×10^{-4} Ω-cm^2 [56].

Metalization using microwave annealing is possible using sintering of metal powers. R. Roy et. al. [6] showed susceptor assisted microwave sintering of various powdered metals to full density was possible using multi-mode microwave oven operating on 2.45 GHz. The cause of better sintering results was attributed to multiple scattering and eddy currents rather than dielectric loss. In 2012, R. Cauchois et. al. [59] showed microwave sintering of conductive silver nanoparticle film, produced using ink-jet printing, could produce resistivity as low as 2.1 μΩ-cm which is very close to bulk silver resistivity of of 1.62 μΩ-cm and the difference was attributed to electron scattering at grain boundaries which was low due to fully dense polycrystalline silver film formation. Further comparison with conventional RTA under similar conditions showed RTA treated resistivity to be 4 to 5 times that of bulk resistivity. This was attributed to partial sintering of the film. Similarly microwave sintering of aluminum powder has been studied by L. C. Chuan et. al. [60]. The study showed densities of 96.22% could be achieved. Thus microwave annealing could have a distinct advantage over conventional RTA for solar cell metalization. Since microwave sintering is able to produce better sintering than conventional RTA, low cost alternative metals, like copper [61], with poorer conductivity than of silver could also be explored. As silver nitride is poor absorber of microwave, percolating network formation may be hindered using microwave annealing, however microwave drilling effects could be utilized at this stage to overcome any issues related to poor formation of of percolation network. Oxide formation on metal surface due to high temperature involvement in presence of oxygen may pose significant problem for microwave annealing. Preferred solutions for this problem could be use of N_2 ambient or exploration of microwave heating under vacuum and lower power.

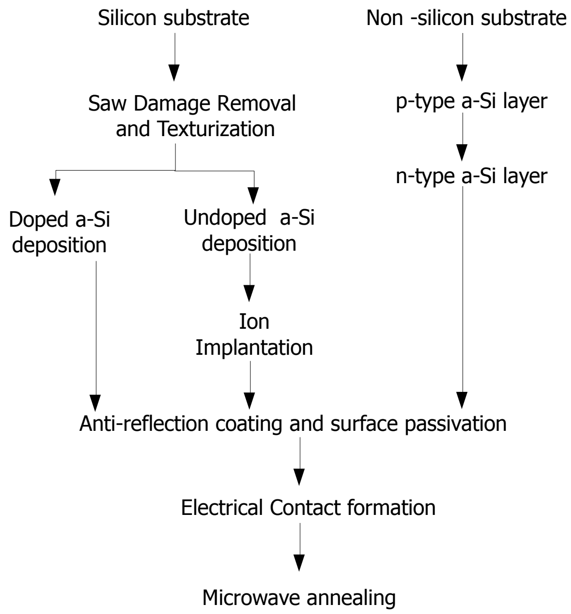

Figure 7. Formation of p-n junction using microwave annealed recrystallization of amorphous silicon method.

V. Synthesis of nanomaterials using microwave heating

Nanomaterials are being increasingly utilized in solar cell research for various purposes. Different forms of nanomaterials could be synthesized with many different methods. Preparing metal nanoparticles using microwave heating is possible. Most common method of nano particles preparation is reduction of metal salts in aqueous solution and reduction could be done with microwave heating alone [62, 63]. Microwave heating limits the use of reducing agent making the fabrication process cleaner and extraction of nanoparticles becomes easier due to absence of chemical byproducts from reducing reactions. Other nanomaterials can also be grown using microwave heating. Differential microwave heating sublimation-sandwich method can be used for growing SiC nanowires [19]. However, these nano wires had a pointed tip (cone shaped). U. O. Mendez et. al. have shown nanomaterials such as nanotubes, nanofibers and microparticles of graphite, sucrose and boric acid can be prepared using microwave heating [64]. T. Krishnakumar et. al. have synthesized flower shaped zinc oxide nanostructures using microwave heating [65].

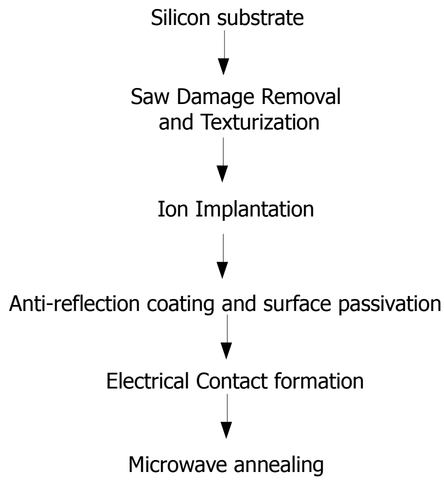

Figure 8. Method of monocrystalline p-n junction formation using microwave annealing.

VI. Microwave Silicon Solar Cell fabrication Schemes

Solar cells using microwave annealing could be introduced using different schemes:

1. Recrystallization of ion implanted amorphous silicon (Fig. 7). Advantage of this scheme is that thin film solar cells could be made on non silicon substrates as well. For a non silicon substrate both n-type and p-type a-Si layers have to be deposited one after another. Recrystallization step can be employed at this stage or alternatively could be avoided till microwave annealing step after electrical contact formation. Later method is shown in the figure as this method could potentially save energy and cost by utilizing only one microwave annealing step. For silicon substrate, doping step could be done during a-Si deposition; or if ion implantation is adopted then recrystallization step could employed after ion implantation or at microwave annealing step after electrical contact formation. The first method could be better choice as lot of studies have been carried out on recrystallization of ion implanted a-Si.
2. Second scheme is microwave annealing of ion implanted silicon wafer (Fig. 8). This scheme is similar to commercial silicon solar cell production except doping is not carried out with $POCl_3$ diffusion method but using ion implantation method. Here again there is a choice of employment of microwave annealing twice or once.
3. The third alternative scheme could be just replacement of contact annealing step of commercial manufacturing with microwave annealing to attract the benefits of microwave annealing. In this method $POCl_3$ diffusion step will need to be adjusted for required junction depth according to diffusion of dopant under microwave annealing.
4. Fourth scheme could be to use point contact microwave applicator for selective emitter silicon solar cells (Fig. 9). In this scheme one could either use ion implantation or $POCl_3$ diffusion for junction formation followed by selective doping step using point contact method. Further steps in fabrication can be to follow last three steps of commercial processing or second scheme.
5. Third generation solar cells are low cost high efficiency solar cells. Plasmonic is an interesting approach to enhance efficiency of these solar cells. In this approach metal nanoparticles, which support surface plasmon modes, can be used to couple light with underlying optical modes of the semiconductor (dielectric) [66, 67]. Thus more light can be coupled to the solar cell, which increases its efficiency. Microwave heating could be used for making the metal nanoparticles and then one can follow many different topologies to make the solar cells [68 - 70]. Other techniques to enhance absorption or reduce reflection to increase efficiency also uses nanostructures. Silicon nanowire solar cell is one such topology [71]. Impedance matching or refractive index matching between surface of the solar cell and ambient is another technique. This could be done using nanowire or nanocone arrays [72] or multilayered anti-reflection coating were

refractive index could be controlled by composite materials of nanomaterials embedded in dielectric matrix. Microwave heating cold be used for both nanomaterial synthesis and embedding purposes.

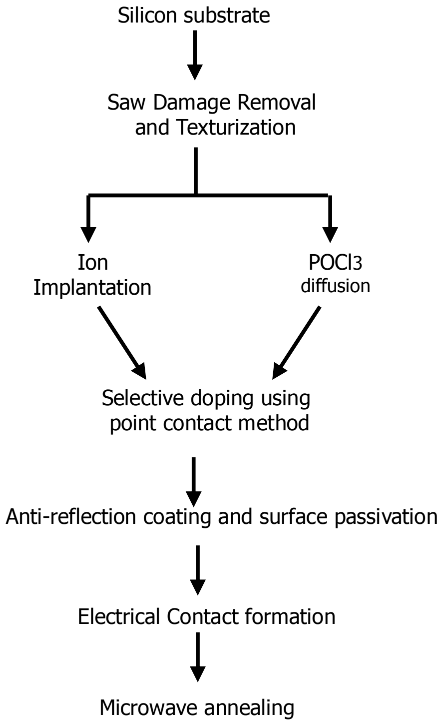

Figure 9. Selective emitter silicon solar cells using point contact method.

VII. Conclusion

In this paper prospects of microwave heating in silicon solar cell fabrication has been reviewed. Purpose of introduction of such technology would be to introduce more sustainable technology for fabrication of silicon solar cells. Five different schemes of fabrication of solar cells have been introduced and for each step, possibilities of such applications have been explored; particularly, in the area of junction formation, metalization, and nanomaterial synthesis. Review of technology for such steps using microwave heating suggested definite possibilities exit for microwave heating to be incorporated in solar cell fabrication process. Further, sustainability analysis of microwave heating was carried out which showed it is more sustainable than conventional heating systems which is a compelling argument to involve microwave heating in manufacturing of renewable products such as silicon solar cells.

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