CHAPTER – II

REVIEW OF WORK ON ELECTRICAL AND PHOTOVOLTAIC PROPERTIES OF POLYCRYSTALLINE -Si AND -GaAs MATERIALS AND THIN FILMS

2.1 INTRODUCTION

In the past few years the search for alternative sources of energy has received much attention. Since the conventional sources of energy; fossil fuels, natural gas and petroleum are fast depleting. The generation cost of electricity from thermal and nuclear sources is also increasing day by day. On the other hand, the electricity from the sun obtained by the solar cells is free of cost, clean, and inexhaustible. Semiconductors in pure, polycrystalline and amorphous forms have been used to fabricate solar cells. Polycrystalline Silicon and Gallium Arsenide are the best materials for the conversion of solar energy into electrical energy. For this reason electrical and photovoltaic properties of these materials must be explored extensively. Several theoretical and experimental studies have demonstrated that the grain boundary, grain boundary interface states, grain size, doping density, temperature and bulk diffusion length of minority carriers etc. influence the electrical and photovoltaic properties of these materials. In this chapter, the existing theories on electrical and photovoltaic properties of polycrystalline Silicon and Gallium Arsenide have been reviewed.

2.2 REVIEW OF THE WORK ON ELECTRICAL TRANSPORT PROPERTIES OF POLYCRYSTALLINE SEMICONDUCTORS IN DARK
2.2. (a) POLYCRYSTALLINE SILICON

Theoretically the potential of polycrystalline thin film solar cells have already been proven, out of which silicon, gallium arsenide, cadmium telluride etc. have found prominent place. A lot of work has been done on polycrystalline silicon in particular. In semiconductor materials one studies the electrical effects of the grain boundaries. The metallurgical aspects of grain boundaries have been developed historically from work on dislocations in crystals. Shockley and Read [45] and Cottrel [46] developed the dislocations model of grain boundaries. The grain boundaries have been divided into four categories viz. [i] Small angle symmetrical tilt boundaries with parallel edge dislocations. [ii] Small or medium angle non-symmetrical grain boundaries of more than one family of dislocations. [iii] Medium angle symmetrical tilt boundaries with contracted edge dislocations and [iv] Large angle incoherent grain boundary areas in which there is no continuity along lattice rows.

For an inhomogeneous semiconductor Volger [47] in 1950, proposed his first model in which he assumed that it is composed of grain boundaries that have difference in resistivity and mobility. Taylor et al. [48] studied experimentally the electrical properties of grain boundaries in group IV semiconductors. They postulated the existence of trapping levels in the forbidden band of grain boundary plans. The electrical conduction at the grain boundary layer was considered mainly due to thermoionic emission of majority carriers. Shockley [45] introduced the concept of ‘dangling bonds’ and ‘broken bonds’ at the grain boundaries in semiconductors. The observations of Mueller [49] were found to be quite consistent with Taylor et al’s work. He suggested that
mainly the thermoionic emission and generation recombination processes control the current over the depletion region of the grain boundary.

As already mentioned in Chapter-1, Kamins [11] proposed the qualitative “Carrier trapping model of polycrystalline silicon”. This model assumes the existence of trapping states in grain boundary region, which are capable of trapping the free charge carriers there by explaining the variation in carrier mobility of polycrystalline silicon with dopant concentration. This model was supported by Rai Choudhary and Hower [12]. The dopant segregation model was developed by Fripp and Slack [13] and Cowher and Sadgwick [14] to explain the conductance of polycrystalline silicon with the doping density. However this model failed to explain the temperature dependence of resistivity and mobility minimum at critical doping density. Seto [15] developed a comprehensive model for carrier transport by using the Kamins carrier trapping model. He treated the grain boundary potential barrier as a metal semiconductor Schottky barrier and assumed complete depletion of grains. However this could not be applied to grains larger than 600 Å. Baccarani et al. [19] modified this model to include the possibility of partially depleted grains. Korsh and Muller [50] considered the grain boundary as a symmetrical semiconductor-to-semiconductor junction. Seager and Castner [17] studied the electrical transport properties of doped polycrystalline bicrystals with partially depleted grains only.

Pike and Seager [51] studied the dependence of barrier height on the applied voltage, whereas Martinez and Piqueras [52,53] developed a model to consider the thermionic field emission of charge carriers along with thermionic emission over the grain boundary region. On the other hand Lu et al. [54,55] provided a conduction model based on semiconductor–grain boundary–
semiconductor type of barrier and investigated the effects of doping density, grain size and temperature on the electrical properties of PX-Silicon. They introduced two artificial factors to fit the theory with experimental data. The modified Lu et al. model [56] considered carrier tunneling as a mechanism of carrier transport across the grain boundary. They considered a rectangular potential barrier $q(\chi)$ so that the maximum potential barrier at the grain boundary is expressed by

$$qV(x) = qV_g + q(\chi) \quad \text{for } 0 \leq |x| = \delta/2$$

(2.1)

This model also had some limitations. The major limitation of their model was that it could not explain the dependence of resistivity on temperature below the room temperature. Furthermore, the grain boundary effects at high doping levels in n-type silicon could not be explained by their theory.

The theories mentioned so far have considered only the carrier-trapping model and neglected the highly disordered nature of the grain boundary. Mandurah et al. [34,35], in their model considered the grain boundary as an intrinsic wide band gap ($E_{gb}=1.32$ eV) semiconductor forming a heterojunction with the grains. They predicted the electrical conduction through grain boundaries due to a combined mechanism of dopant segregation, carrier trapping and carrier trapping through the potential barrier of height $q\phi$. This model explained the dependence of electrical resistivity on doping density, doping species and high temperature processing history of the polycrystalline films. Their model explained the conduction over the potential barrier without considering the thermoionic field emission through the space charge potential barrier $qV_g$ which is very important at low temperature and high doping levels. Wu and Yang [57] proposed a theory of phonon-assisted transition of majority
carriers across the grain boundary. Wu and Ken [58] then proposed a conduction model by including the majority carrier diffusion and grain boundary scattering effects. Peisl [59], and Kim and Khondker [60,61] also presented a new conduction model to explain the conduction of charge carriers across the grain boundary.

Joshi and Srivastava [62] developed the electrical conduction model in which the grain boundary was considered as a rectangular potential barrier of height \( q_\phi (= 0.16\text{eV}) \) at room temperature Fig. 2.1. The maximum potential barrier height in the grain boundary region was expressed by

\[
qV(x) = qH = q_\phi \quad \text{for } q_\phi > qV_g
\]

and

\[
qV(x) = qH = qV_g \quad \text{for } qV_g > q_\phi
\]

They explained the electrical properties of polysilicon by considering all the three mechanisms of carrier transport across the grain boundary. \( q_\phi \) was assumed to be independent of doping concentration, dopant species or grain size. However this model could not explain the resistivity of polysilicon at very low temperatures. Rodder and Antoniadis model [63] considered a new mechanism of two step tunneling of the grain boundary potential barrier and neglected the scattering effects of grain boundary material. However the scattering effects may be the dominant processes at low temperature range especially when the doping level is high [64].

Another model, considering the two step tunneling was developed by Negi and Joshi [65]. They assumed the grain boundary potential barrier \( q_\phi \) as a function of dopant species, temperature and annealing temperature but not a function of grain size, particularly for Boron doped samples of polysilicon. The electrical properties of this material have also been studied by Tyagi and Sen
Fig. 2.1  Energy band diagram near a GB interface under zero-bias condition
(a) Lu et al. model [54]
(b) Mandurah et al. model [34].
[66], Mathur et al. [67], Bhatnagar [68], Hwang et al.[69], Lhermite [70], Seager et al.[71], and Joshi and Wood [72]. Recently a large-bias conduction model has been developed by Das and Lahiri [73]. Groot and Card [74] studied the carrier transport at low temperature and high doping levels and established that it is necessary to include both thermoionic emission and thermionic field emission of trapped majority carriers at the grain boundary states. However the segregation of free carriers is considered as a major mechanism of grain boundary region by Mandurah [33]. On the other hand a study of Deen et al. [75] predicted that the resistivity of heavily doped polycrystalline silicon by phosphorus and boron increases with temperature and current density while that of arsenic doped samples decreases.

Werner [76] proposed a method for the evaluation of grain boundary density of states. His study revealed the dominance of band tail states in bicrystals and fine grained films. Kato and Amemiya [77] presented a physical model to explain the mechanism of resistance decrease in heavily doped polysilicon resistors. In their model grain boundary layers are considered to be having amorphous like structures. Ling [78] derived a current voltage relation across the grain boundary of polycrystalline silicon by considering a diffusion transport mechanism and a constant inherent mobility.

Electronic transport at grain boundaries in large grain cast silicon (SILSO) is experimentally studied by McGonigal et al. [79]. They found a continuous interface states density in $10^{15} - 10^{16} \text{ cm}^{-2}\text{eV}^{-1}$ range for the lower part of the p-type silicon energy gap. The GB potential height $qV_g$ is also measured. Thomson and Card [80] observed experimentally that the diffusion potential at the grain boundary in cast silicon might in many cases exhibit appreciable
variation over the grain-boundary plane. They explained this observed variation in terms of Gaussian distribution of interface states. The dependence of recombination current and barrier height on the excitation level is studied by Palm [81] by using electron beam induced current (EBIC). The experimental results are explained by modifying Seager’s model [82].

Lhermite et al. [83,84] computed $qV_g$ in PX-silicon films by numerical integration of Poisson’s equations. Their studies have shown the conditions of validity of abrupt depletion layer approximation. A correlation between electrical properties and grain size increase in PX-films after LASER annealing for different power and scan rate conditions is studied by Ternisien d’Ouville et al. [85]. Upreti and Singh [86] considered the effect of GB width on the electrical properties of PX-Si films. They proposed a model of average carrier concentration for these films. However their carrier transport model considers only thermionic emissions of charges over the potential barrier at the grain-boundaries. Ramesh and Bhat [87] used resistivity model to determine phosphorus diffusivity in PX-Si.

2.2. (b) GALLIUM ARSENIDE

The importance of low cost polycrystalline film of GaAs for solar cells has been outlined by many workers [88,89]. Polycrystalline GaAs can be an economic choice for solar cells since it can be grown in thin film form. In the past, less attention was given to the research work on devices related to GaAs due to low availability of this material. However, in recent years, the wide application of GaAs in microwave and optoelectronic devices has grown rapidly. It has been proved that GaAs can be grown both as a single crystal and polycrystalline film with controlled thickness to the doping bands up to $10^{19}$ cm$^{-3}$.
When this material is grown on substrates like graphite, the film grown is often polycrystalline and not single crystalline [90].

The presence of two elements and the factor of stoichiometry make the study of GaAs much more difficult than the widely studied polycrystalline silicon. Consequently, very little information is available regarding the electrical properties of polycrystalline GaAs thin films. The work of Dupuis et al. [91] showed that the resistivity of polycrystalline GaAs is 2 to 3 orders of magnitude higher than that of single crystal materials of the same doping level. The study of Chu et al. [92] found that the average grain size of GaAs film increases with the increase in film thickness and is about 5 µm in 8-10 µm thick film. It was also noticed that at substrate temperature 725-750 °C, the grain size increases with Arsine concentration in the reactant mixtures. Other workers [93,94] have also studied the dependence of carrier concentration on substrates temperature of Arsine/Hydrogen molar ratio.

Yang et al. [32,95] performed a thorough experimental study of the variation of resistivity with free-carrier density for MO-CVD deposited polycrystalline GaAs films (both n- and p-type). The resistivity and mobility have been observed to be temperature dependent over a wide temperature range. These results have been explained analytically by considering grain boundary scattering effects. They assumed that the Hall coefficient was a measure of average free carrier density. It was observed that the resistivity and grain-boundary barrier height of n-GaAs films were higher than that of p-GaAs films. Yang et al.’s measurements of resistivity and carrier concentration for PX-GaAs films were based on the assumption that the carrier mobility was spatially constant in these films. However, it is shown by many workers that for
polycrystalline materials this assumption is not correct, especially when doping density is of the order of \(10^{16}\) cm\(^{-3}\). Their studies predicted that the free carrier density was independent of sample temperature. However, this prediction seems to be inconsistent with the study of many workers.

Recently Epple et al. [96] examined the electrical properties of PX-GaAs grown by MBE (molecular beam epitaxy) and PX-GaAs formed by annealing amorphous GaAs also grown by MBE. It was noticed that a:GaAs becomes highly conductive upon annealing. The conduction of materials annealed at temperatures in the vicinity of 400 °C is believed to be the result of excess arsenic, acting as a semi metal forming a continuous network between GaAs grains.

### 2.3.1 GRAIN BOUNDARY RECOMBINATION AND ELECTRICAL PROPERTIES OF POLYCRYSTALLINE SEMICONDUCTORS UNDER OPTICAL ILLUMINATION

The polycrystalline semiconductors are composed of grains and grain boundaries. The grain boundaries act as a recombination centers for the minority carries and as potential barrier for majority carries. These adverse effects of impedance and recombination become more complicated when a polycrystalline material is doped heavily with impurity atoms and subjected to optical illumination. Under optical illumination the photo generated minority carriers are attracted towards the grain boundary by the depletion layer field, where they neutralize the majority carriers trapped by the grain boundary and thus reduces space charge potential barrier height \(qV_g\) from its dark value. In the past, several theoretical models [82,97,98] mainly in the framework of one dimensional equations and boundary conditions have been proposed to describe the influence of grain boundary on minority carrier transport and recombination.
The first recombination theory at grain boundaries in a rectangular semiconductor filament was proposed by Shockley [99]. He deduced an expression for the filament lifetime by solving two dimensional transport equations. The recombination processes at grain boundaries in polysilicon was first studied by Card and Yang [100] by using an S-R-H recombination theory. They considered a uniform distribution of grain boundary states in the energy gap and predicted that \( qV_g \) decreases with increasing illumination level (G). This model was based on the quasi-equilibrium assumption, which is generally not valid. This assumption holds well only when \( qV_g < 0.2 \text{ eV} \) [82,97]. They also studied the dependence of effective recombination velocity and minority carrier lifetime on the doping concentration, grain size and interface states density at the grain boundaries. This model was also used by Kazmerski [101] to study the grain boundary recombination mechanism in other polycrystalline semiconductors.

Panayotatos and Card [102], and Hwang et al. [103] considered exponential, uniform and monoenergetic distributions of grain boundary states. These models were not based on quasi equilibrium condition. They calculated the extra charge developed due to acceptors and donors by integration over corresponding density of recombination centers. During the process of recombination under optical illumination, the induced separation of electron and hole quasi-Fermi levels was observed to be directly proportional to the carrier concentration at the grain boundary. In their study they did not consider equal capture cross-sections of grain boundary states for samples having large \( qV_g \).

Poon et al. [104] developed a model based on the Gaussian distribution of grain boundary states. Their study suggested that \( qV_g \) should always
decrease with increasing illumination level, whatever is the range of the illumination level. Studies of Seager [82] and Kazmerski [98] suggested that this prediction is not always true. Card [105] studied the dependence of $qV_g$ on illumination level and grain size by assuming uniform photo generation rate in cubic grains and neglecting bulk recombination of minority carriers. One of the limitations of his analysis is that it cannot be applied to large grain size polysilicon. Makino and NaKamura [106] found experimentally that the photoconductivity of PX-silicon increases by plasma annealing. They estimated the lifetime of minority carriers from the value of photoconductivity measurements.

Seager [82] proposed a detailed theoretical model for the grain boundary recombination under optical illumination. He considered uniform generation of light induced carriers, low injection levels and depletion approximation. His model permits the variation in minority carrier quasi-Fermi level with distance in the grain boundary space charge and the bulk regions. He also suggested the transport of majority carriers from the quasi-neutral region of grains to the grain boundary by the thermionic emission. He studied the dependence of $qV_g$ and $S(W_g)$ on illumination levels for polysilicon bicrystals and predicted that for $qV_g < 0.2$ eV and high illumination level the quasi-equilibrium condition is generally valid within the depletion region. His computed results agree well with his measurements. The main inadequacy of Seager’s model is that it does not consider the dependence of $qV_g$ on grain size.

The Fossum and Sundaresan model [107] based on quasi-equilibrium assumption provides a valuable insight into the grain boundary recombination mechanisms. They had considered both donor and acceptor like recombination
centers in the energy gap of the grain boundary; furthermore they had considered a monoenergetic distribution of grain boundary states near the midgap. In their studies they established that $qV_g$ is not dependent on illumination level and grain size. They also did not use the depletion approximation in the space-charge region. They predicted that the value of $S(W_g)$ for silicon is not infinite but is equal to $1 \times 10^6$ cm/s at 300K. Orton et al. [108] suggested that trapping of photo generated carriers decreases the effective charge of the grain boundary, resulting in lowering of potential barrier and increasing the photoconductivity.

Landsberg and Abraham [109] considered a $\delta$-function distribution of energy states of the GB, the quasi-equilibrium assumption and infinite recombination velocity of minority carriers and neglected bulk recombination. However in general these assumptions are not valid. They studied the variation of $qV_g$ with doping density, illumination level and interface states density. Ling [78] model considered diffusion mechanism to study the carrier transport across the grain boundary. The variation of $qV_g$ with excitation level has been studied by Qualid et al. [110,111]. Their theory assumed uniform energy distribution of grain boundary states and neglects bulk recombination of photo-generated carriers. However, the bulk recombination process can’t be neglected in the large grain size range [82].

Dimitriadis et al. [112] proposed a model by considering equal capture cross-section of grain boundary states for electrons and holes. They investigated the effects of $qV_g$ on illumination levels and grain size. Their prediction that $qV_g$ decreases continuously with increasing grain size (even in large grain size range) is not in agreement with the studies of Joshi et al. [113,114]. Joshi [114]
studied the dependence of $qV_g$ on grain size, bulk diffusion length and illumination level. His theory considers bulk recombination of minority carriers by using monoenergetic distribution of grain boundary states. This model predicts that $qV_g$ and $S(W_g)$ are independent of grain size in the large grain size range. Though, this analysis does not take into account the quasi-equilibrium assumption. Mohammed [115], and Mohammed and Rogers [116] studied the grain boundary recombination processes by considering drift and diffusion of minority carriers and variations of $qV_g$ and $S(W_g)$ with illumination levels. Their study considers non-uniform generation of minority carriers. However they did not compare their results with the experimental results.

Joshi and Bhatt [117,118] presented a comprehensive recombination model for polysilicon under optical illumination. Their study was based on Gaussian distribution of GB states. They suggested that the GB effects do not remain limited to the grain boundary depletion region but extends up to the quasi-neutral and neutral regions of the adjacent grains. Some of the above mentioned GB recombination models are found to be the special cases of this model. The dependence of $qV_g$ on grain size, illumination level and bulk diffusion length is also investigated. Bhatnagar and Verma model [119] on GB recombination is based on [115-118]. The experimental study of McGonigal et al. [79] found that exposure of polysilicon to optical illumination reduces the GB potential barrier.

Ammor et al. [120] studied experimentally the recombination activity of grain boundaries and their passivation by hydrogen in large grained PX-Silicon. They found that dislocations control the recombination activity. Recently Fanying Meng et al. [121] have studied theoretically the recombination properties of
grain-boundaries in PX-Si under optical illumination. Their model is based on Gaussian energy distribution of GB states. They have investigated the influence of doping density on the GB recombination velocities and recombination current density at the GB.

Negi et al. [122] proposed a carrier transport model for PX-Silicon under optical illumination by considering [65] model and including Two-Step-Tunneling (TST) process at the grain boundary states to explain the temperature dependence of the electrical properties of this material.

### 2.3.2 ELECTRICAL PROPERTIES OF PX-SEMICONDUCTORS UNDER OPTICAL ILLUMINATION

Only a few papers are available predicting the electrical properties of polycrystalline materials under optical illumination. Maruska et al. [123] presented a qualitative model to explain the effective mobility of polysilicon by using a diffusion model for carrier transport. In this model a complete elimination of $qV_g$ at 1 SUN illumination was considered. The experimentally measured mobility is in the 100 to 400 K temperature ranges. They found a $T^{-2}$ dependence in low temperature range and $T^{-3/2}$ dependence over the high temperature range. They neglected the GB scattering effects; however their model failed to explain the dependence of carrier mobility on temperature in the low temperature range.

Carrier transport in polysilicon under optical illumination was extensively studied by Card et al. [103,105]. They assumed that thermionic emission was a dominant current mechanism in the GB region. They found that bulk photoconductivity in polysilicon is a majority carrier phenomenon and it increases with the grain size. However, their model could not explain the temperature dependence of electrical properties of this material.
Groot et al. [74] predicted that for the carrier transport across the GB, both thermionic emission and thermionic field emission components must be considered. It was also found that the grain boundary interface states distribution is controlled by temperature. Card [124] explained the photoconductivity of polysilicon by considering equal effective cross-sections for electrons and holes. Orton et al. [108] used Seto model [15] to explain the photoconductivity of CdS films. They considered grains as cylinders of radius ‘a’ and infinite height. Panayotatos et al. [125] determined the grain boundary recombination velocity under illumination from photo-conductance measurements. It was observed that different points on the same grain boundary have different response.

Joshi and Srivastava [126-127] produced a first quantitative conduction model by considering the grain boundary scattering effects. They explained the dependence of qVg on grain size, doping level and illumination level. This model has satisfactorily explained the dependence of electrical properties of PX-Silicon under illumination on temperature. However, qVg was assumed to be zero in this model, and was applicable only for large grain sizes under high illumination level. Tyagi and Sen [128] considered the theory of capture-emission carrier processes at GB, whereas Dimitriadis et al. [112] also used the same concept [128] to explain the electrical properties of polysilicon under illumination. However these models [112, 114] have some inadequacies.

Bhatt and Joshi model [64] have studied the electrical properties of PX-Silicon by considering GB scattering effects, variable range hopping of carriers in the grain boundary states and all the three carrier transport mechanisms TE, TFE, TFES. This model was valid for all grain sizes. However, it is found that variable range hopping mechanisms does not suitably explain the
electrical properties of this material in very low temperature range. Hinckley and Gluszak [129] studied the effects of depletion layer recombination in polycrystalline photovoltaic devices under illumination. The flux method has been used to stimulate the effects of depletion layer and grain boundary recombination on the performance of PX-silicon solar cells. Thus there is no electrical conduction model to explain the electrical properties of polycrystalline semiconductors in dark and under optical illumination comprehensively. The present work is an endeavor to fill in the gap between theory and experimental work.

2.4.1 PHOTOVOLTAIC PROPERTIES OF POLYCRYSTALLINE SEMICONDUCTOR SOLAR CELLS; PX-SILICON

The large number of defects and segregated impurities at grain boundaries in polycrystalline semiconductors become regions of strong recombination centers. The recombination at the grain boundaries decreases the photo current and enhances dark current of the device and shortens the effective diffusion lengths of minority carriers. Consequently, the efficiency of polycrystalline solar cell is decreased. The reduction in photovoltaic parameters $J_{sc}$, $V_{oc}$ and FF by the recombination processes is strongly dependent on grain size in the polycrystalline layers. In the past, several experimental and theoretical works has been performed on the role of grain boundaries and their effect on photovoltaic properties of semiconductors. Some of the work done so far is reviewed below.

Soclof and Iles [130] considered the grain boundary as perfect sinks for excess minority carriers. They studied the variation of diffusion length, short circuit current and cell efficiency with grain size, however $V_{oc}$ was considered to
be independent of grain size. Rothwarf [131] by establishing a simple recombination model studied the effects of grain boundaries of PX-solar cells to estimate $J_{sc}$. He assumed that all carriers generated near the grain boundary were lost.

Card and Yang [100] developed a GB recombination model to consider the effects of illumination on GB potential barrier and the recombination processes by using the S-R-H model. They calculated the effective lifetime ($\tau_{\text{eff}}$) of the minority carriers using Shockley [99] concept of filament lifetime. They did not assume infinite recombination velocity at the grain boundaries. However their model failed to explain the dependence of cell efficiency on grain size in the large grain size range. Green [132] focused his attention on the role of grain boundaries by considering a three-dimensional equivalent circuit approach instead of solving the differential equations governing the carrier transport. He observed that the grain boundaries parallel to the junction caused a severe loss to the photocurrent while those perpendicular to the junction were least detrimental to the photocurrent. His study also investigated that the grain boundaries had a little effect on photocurrent if $d > L_b$. The results of his theory were well in agreement with the experimentally observed facts of Fischer and Pschunder [133].

Koliwad and Daud [134] assumed that each grain was composed of two parts; a central part having constant diffusion length and a surrounding part having a variable diffusion length $L(z)$ which varies from 0 to $L_b$. by using the empirical model for effective diffusion length $L^*$, they computed the variation of $J_{sc}$ with grain size ‘$d$’. It was predicted that the efficiency ($\eta$) would increase from 30 to 32% with the increase in grain size from 100 to 1000 $\mu$m. This model had
many drawbacks, e.g. it required an artificial factor ‘f’ in order to fit the experimental data with theoretical predictions and no attempts were made to compare the values of $V_{oc}$ and FF with the experimental data. Lanza and Hovel [30] solved the three dimensional transport equations within cylindrical grains to study the variation of cell efficiency ($\eta$) with grain size. Modified analysis of Lanza and Hovel [31] considered $qV_g = 0.2$ eV and assumed effective lifetime $\tau^*$ to be independent of grain size. They also calculated the depletion layer width at GB in the top and base region of the cell. Makran-Ebid [135] solved the two dimensional transport equations in a PX-silicon solar cell. They studied the variation of spectral response with illumination levels. They observed 18% increase in the spectral response in a Si solar cell at 0.875 $\mu$m when it was flooded with 1 SUN of AM1 illumination.

Ghosh et al. [136,137] developed an empirical relation for $\tau^*$ to explain the performance of PX-silicon cells. They found that whatever be the shape of grains, solar cells with 10% efficiency at AM1 condition could be produced by using 20 $\mu$m thick films having grain size larger than 500 $\mu$m. Their computed results were in good agreement with the experimental data. However, they assumed complete elimination of $qV_g$ under AM1 conditions and a substantial shrinkage of junction depletion layer was observed under illumination. Fossum and Lindholm [138] in their analysis included the GB effects within the junction depletion region and found that the recombination current density for a columnar grain follows $\exp(qV_g/kT)$ dependence. Their work was consistent with the work of Henry et al. [139]. Their theory for PX-silicon in dark conditions found that $\tau^*$ had a $d^2$ dependence for high values of grain boundary recombination velocity. A
similar type of dependence of $\tau^*$ on $d$ was established by Sopari [140]. These analyses [137,141] however are not applicable to illuminated solar cells.

Cheek et al. [142] developed a model of ITO / polysilicon solar cell as an inversion layer device and noted a rapid rise in $J_{\text{sc}}$ and FF on decreasing insulator layer thickness from 20 to 15 Å. The cause in this variation was attributed to the exponential change in tunnel current with thickness and the transition from the tunnel current limited mode to the semiconductor limited mode. Anderson et al. [143] studied chromium metal polysilicon (MIS) solar cells to determine the current flow mechanisms. Their study indicated a surface state controlled current for $T > 150$ K and tunneling controlled current at lower temperatures. Rajkanan and Anderson [144] computed efficiency as a function of the grain size, doping concentration and the oxide thickness. Almost linear variation of efficiency with grain size was reported. They also studied loss mechanisms in MIS solar cells.

Card and Hwang [145] investigated theoretically the effect of grain boundaries parallel to the junction plane on the carrier in Schottky barriers. The effective diffusion length of minority carriers was found to be increasing with increase in bias voltage and grain size. Yang et al. [146] discussed the effect of non-columnar grains on the current-voltage characteristics of PX-silicon solar cells. They found that the grain boundaries perpendicular to the junction plane have little effect on the majority carrier transport. Kumari et al. [147] studied the variation of $p^+\text{-}n\text{-}n^+$ PX-silicon solar cell parameters with grain size in the range of 0.3 to 3mm. The space-charge recombination reverse saturation current was found to increase at least by three orders of magnitude over the given grain size range. The variation in diffusion length within the grain was also studied. Bohm
et al. [148] determined the influence of recombination velocity and grain size on the spectral response and photocurrent of a PX-Silicon by solving the two dimensional diffusion equations for minority carrier transport within individual grain. Halder and William [149] derived relationship between photocurrent and dark current by using Green’s function and solving three dimensional diffusion equations for minority carriers. A major limitation of this analysis is that it is based on superposition principle of dark and photocurrent; So et al. [150] simplified the three-dimensional network of GB interface states to a one-dimensional distribution of bulk traps to characterize the photovoltaic properties of PX-Silicon MIS solar cell. They assumed PX-Si as a homogeneous material. Several other workers [151,152] have studied the performance of MIS and SIS solar cell devices.

Joshi and Srivastava [113] proposed a relation for effective diffusion length $L^*$ and found the dependence of $L^*$ as $d^r$ where $r$ lies in the range of 0 to 1. They investigated that efficiency is a strong function of grain size for the grains of size smaller than $L_b$. Mohammed et al [116] presented a theoretical model and derived new formulae for $J_{sc}$, $V_{oc}$ and FF and efficiency with regard to n$^+$$-$$p$ polycrystalline solar cell and predicted that the highest values of solar cell parameters depend on some optimum value of the grain size and doping level. Dimitriadis [153] investigated theoretically the effect of doping density on the efficiency of solar cells. He predicted that efficiency of PX-silicon solar cells will be maximum in the doping range $10^{16}$ - $4 \times 10^{16}$ cm$^{-3}$, when $N_{gs}$ lies in the range $10^{11}$ to $10^{13}$ cm$^{-2}$. Their work was based on Seager’s model [82]. Dugas and Qualid [111] proposed a three-dimensional model for PX-Si cells. They found that the cell efficiency could be improved by optimizing the doping concentration.
of the base region, which was found to be a function of grain size and GB states density. In their model the effect of device thickness and variation in $qV_g$ with grain size were not considered. Bhatt and Joshi [154] studied the dependence of $L^*$ and other parameters on the grain size and doping level of a PX-Silicon solar cells. It was demonstrated that such a cell with 10% efficiency at AM1 condition could be fabricated only if the thickness of the device and grain size are greater than bulk diffusion length (100 $\mu$m) and $qV_g$ is less than $2kT/q$. However the distribution of GB states was not studied in their work. Okamato et al. [155] fabricated solar cells on polycrystalline substrates. Matsukrme et al. [156] obtained 15.2% efficient solar cells experimentally by the hydrogen passivation technique. Markvart [157] used Green's function formalism to obtain relationship between spatial dependence of solar cell parameters in dark and under illumination. Green [158] describes the dependence of effective lifetime of PX-silicon on GB geometry and activity. The calculations of Green [158] demonstrated that GB effects in both depletion and quasi-neutral region of solar cells could be bounded by introducing an effective lifetime parameter which depends on the GB geometry and activity. With the help of this approach three dimensional grain boundary effects can be simplified to a one-dimensional equivalent. Nunoi et al. [159] investigated the efficiency of cast PX-Si solar cell with grooved surface experimentally. The cell surface is mechanically grooved and chemically etched. The grooved surface minimizes the reflectance. It is found to improve short circuit current by 4% and efficiency by 1% compared with the textured surfaced PX-Si solar cells.

Imaizumi et al. [160] have studied the dependence of solar cell parameters on film thickness and grain size. It was demonstrated that thin film
polycrystalline solar cells have the potential to attain efficiency up to 17% even at film thickness 10 µm and etch-pit density less than $10^6$cm$^{-2}$. Comparison of minority carrier diffusion length measurements in PX-Si solar cell by photo-induced open circuit voltage decay (OCVD) using different LASER excitation sources has been studied by Stutenaebumer and Lewetegn [161]. The experimental study of Macdonald [162] is concerned with the measurement and interpretation of carrier lifetime in multicrystalline Si solar cells. He developed a new technique “dubbed injection level dependent lifetime spectroscopy (ILDS) to study lifetime of minority carriers in this material.

Recently Rohatgi et al. [163] have predicted that solar cell efficiencies of 18.2% and 17.8% can be achieved with edge defined film-fed (EFG) grown and string ribbon multicrystalline silicon respectively by rapid thermal processing. It was found that bulk lifetime decreases with the increase in annealing temperature above $750^\circ$C.

**2.4.2 POLYCRYSTALLINE GALLIUM ARSENIDE SOLAR CELLS**

The semiconductors suitable for solar cell fabrication are Si, GaAs, CdTe, CdS, CuS and AlSb. However, PX-Silicon and GaAs semiconductors are the most suitable materials for solar cell fabrication. GaAs solar cell is more favorable than Si in the high temperature operation. This cell has high temperature efficiency. The main disadvantage of GaAs is that its raw material is very costly. On the other hand PX-Silicon is the least expensive. Silicon in its bulk, single crystal and polycrystalline forms is the most extensively characterized and best understood material for solar cell technology. It has been demonstrated that efficiency of polycrystalline solar cells is reduced by the grain boundaries in a number of ways [36], such as recombination at GB decreases
the photocurrent and enhances the dark current of the device. GaAs is a direct band gap semiconductor with an energy gap of 1.43 eV at room temperature. Because of its sharp absorption edge and large optical absorption coefficient, relatively short minority-carrier diffusion length can be tolerated in this material. The best studied bulk GaAs solar cell has been the p/n homojunction [2]. Typically GaAs p/n junction was made on polished single crystal wafers doped to form n-type to about $10^{17}$ cm$^{-3}$. Zn and Cd acceptors were diffused to a depth of about 1 µm to form a p-n junction [2,31]. GaAs solar cells have also been fabricated on Schottky barrier and MIS structures.

The use of thin GaAs film on a suitable substrate is also a promising approach for the fabrication of low cost solar cells. As compared to the PX-Silicon solar cells, little information is available regarding the film GaAs solar cells. The first cell using GaAs film deposited by sputtering was reported in 1976 by Vohl [89]. The first theoretical model to understand the physics of thin film GaAs solar cells was proposed by Lanza and Howel [30]. Their calculations on the effects of grain sizes, short circuit current have shown that the AM1 efficiency of thin film GaAs Schottky barrier solar cells can approach to 12% for grain sizes of 3 µm or greater. They assumed a fixed value of $qV_g$ and infinite recombination velocity in their calculation for cylindrical grains. The modified analysis of Lanza and Hovel [31] considered a fixed value of $qV_g$ ($= 0.2eV$) and assumed minority carrier effective lifetime $\tau^*$ to be independent of grain size. However many studies [64,126] shows that $qV_g$ and $\tau$ are function of grain size and illumination level. Thin films of PX-GaAs deposited on tungsten coated graphite substrates were used for the fabrication of MOS type PX solar cells by Chu et al. [40]. The average grain size of these PX-films was 1-2 µm and the film thickness was of
10-20 \mu m range. The efficiency of these cells was found to be about 6.5% at AM1 conditions.

Dapkus et al. [95] prepared PX-GaAs films by Metal-Organic Chemical Vapor Deposition technique (MO-CVD). They found that effective diffusion length in most GaAs films is in the range of 0.5-0.8 \mu m. They studied the electrical properties of PX-GaAs materials and solar cell devices. Efficiencies of 2.25% for Schottky barrier solar cells were reported. They found that the resistivity of both n- and p-type GaAs materials depends on temperature as \( \exp(E_b / kT) \), where \( E_b \) is the barrier height. It was found that the efficiency of a PX-GaAs solar cell is limited by the grain boundaries. Blakeslee and Vernon [165] fabricated Schottky barrier PX-GaAs solar cells by using films of the order of 10 \mu m. These solar cells were having columnar grains. The conversion efficiency of these cells was found to be about 1.3% at AM0. Singh et al. [166] investigated the effect of grain boundaries on the performance of MIS solar cells fabricated on PX-material. The tunneling probabilities of carriers were calculated by WKB approximations and the role of tunneling component was studied. The efficiency of a PX-GaAs solar cell with grain size 4 \mu m was found to be 10%. Turner [28] fabricated a large-grained GaAs homojunction solar cell with conversion efficiency exceeding 13% at AM1 by using passivation techniques. For these cells high value of open circuit voltage of the order of 0.7 V was reported. Gandhi et al. [167] reported an 8.6 \mu m thin-film PX-GaAs solar cell with a conversion efficiency of 5.45% under AM1 conditions made by metal-organic process and on a Molybdenum substrate. They predicted that the performance of these solar cells could be improved by passivation of the grain boundaries. A technique was described by Pande et al. [168] for the fabrication of PX-GaAs
solar cell with grain boundary edge passivation. It was shown that the GB plays an insignificant role in reducing current collection capability of the cell.

It was found by Chu et al. [24] that a ruthenium ion treatment of PX-GaAs MIS Schottky barrier solar cells of surface area 9 cm² reduced the surface recombination velocity and yielded an efficiency of 8.5%. The average grain size of their films was 5 µm and the thickness was 10 µm. Yeh et al. [29] fabricated bulk PX-GaAs MIS solar cells with AMOS (Anti-reflecting Metal Oxide Semiconductor coating) on the sliced PX-GaAs wafer with an average grain size of 100 µm and achieved conversion efficiency of 14% under AM1 illumination condition. They also fabricated PX-thin film GaAs MIS solar cells with efficiency of 8% by vacuum deposition of n-Sb₂O₃ insulating layer. In this case, 2-3 µm thick n-GaAs PX-film was grown on a LASER re-crystallized Ge layer on a W coated substrate. Their study demonstrated that the effect of grain boundaries is most serious on \( V_{oc} \) and fill factor. Chu et al. [26] fabricated MOS solar cells using PX-GaAs films deposited on tungsten coated graphite substrates. They prepared solar cells of 9 cm² area with efficiency of 5.2% without antireflection coating. It was demonstrated that the use of a thin GaAs-phosphide layer on the surface of GaAs film or the use of zinc doping could improve the solar cell characteristics. They predicted that the shunting effects of grain boundaries may be reduced by zinc doping.

A method of combining Schottky barrier electron beam induced current imaging of grain clusters was developed by O.Paz and Borrego [169] for quantitative determination of diffusion lengths of PX-GaAs. They achieved this by comparing the measured number of collected carriers per incident electron to a calculated value. Diffusion lengths measured for PX-GaAs ranged from 0.2 µm
for polycrystalline and bulk single-crystals to 7.5 µm for CVD grown layers. Their theory is valid only when the generation volume is confined within the grains. The MOS GaAs solar cell was studied by Das et al. [170]. The improvement in $V_{oc}$ is attributed to the increase in barrier height due to incorporation of a thin oxide at the metal-semiconductor interface, which modifies the surface states density. The undoped PX-GaAs substrates having carrier concentration $10^{16}$ cm$^{-3}$ have shown $V_{oc}$ of about 0.3 V and $J_{sc}$ of the order of 6mA/cm$^2$.

Yamaguchi and Itoh [171] studied the effects of grain boundaries on the efficiency of PX-GaAs thin-film solar cells by developing a simple model. They found that the grain boundaries reduce the minority carrier diffusion length in the cells active layer and increase the space-charge layer recombination current. The effective diffusion length is expressed in terms of grain size, allowing the calculation of $J_{sc}$ and $V_{oc}$. Excellent agreement was observed between their theory and experiment. The experimental study of Chu et al. [172] found that thin film GaAs solar cells of p$^+$/ n configuration with efficiency of 9.3% and 10.3% respectively at AM1 condition have been prepared by using re-crystallized germanium on tungsten/graphite and large grain size Ge slices as substrates. Solar cells fabricated on large-grain slices have much better electrical characteristics due to the increased grain size. Mohammed et al. [173] developed a theoretical model to study the effect of grain boundaries on the efficiency of n$^+$-p PX-GaAs solar cells. His model was based on the solution of continuity equation and considered the recombination at GB space-charge region and the bulk region of the semiconductor. The grain size in PX-thin films was found to be a very important parameter which influences many physical and electrical properties of solar cells. This parameter is further dependent on crystal
growth parameters viz. temperature, film thickness, annealing temperature and dopant concentration. It was observed that the grain size increases with increasing deposition temperature and film thickness (grain size and doping levels are important device parameters for optimizing the solar cell parameters). The measured values of diffusion length and solar cell parameters are found to be in agreement with the experimental results.

Ringel [174] developed high efficiency MOCVD grown GaAs p-n heterophase solar cells. These cells were characterized to access the loss mechanisms and its design has been optimized through extensive computer modeling. The recombination velocity of the order of $1.25 \times 10^5 \text{ cm/s}$ at the p-n junction heteroface and minority carrier lifetime of 8 ns was observed. A further understanding of loss mechanisms and improvements in device modeling can provide GaAs solar cells with efficiencies approaching 25% under AM1.5 conditions. Venkatsubramaniam et al. [175] demonstrated a high efficiency GaAs solar cell developed on a cast optical grade PX-Ge substrate. Its efficiency was 15.8% which is the highest efficiency ever reported. The study of Kurtz and McConnel [176] reveals the dependence of efficiency of PX-GaAs solar cells on dislocation density, grain size, intragrain defects, impurities and GB defects and predicted that to achieve efficiency more than 20% the dislocation density should be less then $5 \times 10^{16} \text{ cm}^{-2}$ for very large grain sizes. Sotoodeh et al. [177] proposed an empirical mobility model. A detailed physical formulation of various scattering mechanisms has been made to accurately determine the variation of mobility with carrier concentration and temperature. However, their model has some limitations; such as their model is applicable for low field mobility of III-V compounds as a function of doping concentration, temperature and composition.
Modifications are required to use their model at very low temperatures. They assumed that majority and minority carriers have same mobility.

Thus, in order to utilize PX-GaAs and -Si materials to the photovoltaic devices one must understand the carrier transport process across the GB and the carrier recombination processes in the GB region. The review of the existing literature demonstrates that there is a great need to develop theoretical models for these processes.