Thin film solar cells

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Abstract   The principal factor affecting the increased penetration of photovoltaics into the marketplace is cost. For traditional crystalline silicon modules, half of the cost is that of the silicon wafers. As a result much effort has centered on reducing this cost by the use of thin film technologies. Substantial technical progress has been made towards improving the efficiencies of polycrystalline thin film solar cells to reduce the production costs. Progress in semiconductor deposition techniques has also been rapid. The most mature of these are based on polycrystalline silicon (p-Si), amorphous silicon (a-Si), copper indium diselenide CuInSe$_2$ (CIS), and cadmium telluride (CdTe). This paper explores the recent advances in the development of polycrystalline thin film solar cells.

요   약   태양전지가 시장성을 확보하는데 가장 중요한 요소는 전지의 가격이다. 기존의 결정질 실리콘 태양전지에서는 가격의 절반 정도가 웨이퍼 가격이다. 결과적으로 이러한 가격을 줄이기 위해서 박막 제조 기술에 많은 노력이 집중되고 있으며 박막형 태양전지의 효율을 증가시키기 위한 많은 기술적인 발전이 되고 있다. 박막형 태양전지의 기술에 관한 기술 발전은 다결정 실리콘(p-Si), 비정질 실리콘(a-Si), CuInSe$_2$(CIS), CdTe 등에서 주로 이루어지고 있다. 본 논문은 박막형 태양전지 분야에 있어서의 최근의 연구 성과에 대해서 알아보았다.

1. Introduction

The principal requirements to the widespread utilization of photovoltaic power generation are lower costs, higher efficiency and increased reliability of the solar cell. Worldwide annual production of solar cells has reached a level of 70 MW_P in 1993, which is about 15 times higher than a decade ago [1]. Over the same period the cost per peak-Watt decreased dramatically and will continue to fall in manufacturing scale and cell efficiency are increased further and if the cell material usage is reduced further. It has become increasingly clear in recent years that the non-concentrator silicon wafer based technologies, that dominate the present solar power market, would be hard pressed to achieve the cost savings believed necessary to compete with other power generation technologies [2]. To meet this challenge various thin film technologies have evolved. If we examine the available material with an appropriate bandgap, absorption coefficient, minority carrier life time and surface recombination velocity, the choice is limited to such material as a-Si, c-Si, GaAs, CdTe, Cu_2S, InP and $CuInSe_2$. Except for c-Si, all other materials, by virtue of their electrical and optical properties must necessarily be in thin film form. Although the basic physics of thin film devices is the most complex, they offer three important advantages.

1) The material costs remain a small part of the total cost because the required thickness of the active layers is on the order of two or three times the optical absorption length.

2) Thin film process has advantages with respect to large scale application and mass production because several low cost, high throughput and scalable methods such as PECVD (plasma enhanced chemical vapor deposition), electrodeposition, spraying, sputtering and screen printing are available for fabricating the thin film solar cell.

3) Low-cost substrates such as soda lime glass and plastic are used in large-area modules.

The long term cost goals of polycrystalline thin film modules are in the range of $ 50/m^2 [3,4]. At the point of 15 % (150 W_P/m^2) this would mean that module cost would be $ 0.33/W_P.

2. Thin film c-Si solar cells

The use of thin polycrystalline silicon for solar cells offers the potential of capturing the high performance of crystalline silicon while achieving the potential low cst of thin films [5]. The newly emerging crystalline silicon (c-Si) thin film technology offers potential performance advantage over even the established c-Si wafer based technologies such as material saving, reduced material quality, higher efficiency [6], higher radiation resistance [7,8] and less weight [9,10]. In addition, as with other thin film technologies, the potential exists to automate cell fabrication on a mass basis. This combination of the high performance and stability inherent in c-Si with the low cost potential of the

thin film approach makes this technology a promising candidate for a place in a future photovoltaic industry.

Traditional c-Si solar cells are fabricated on commercial silicon wafers 300 ～ 500 μm thick. Such dimensions provide mechanical strength, and are necessary to ensure sufficient absorption of the incident sunlight, with silicon only a weak absorber of the longer wavelength components of this light. Recent advances in light trapping, a process in which the weakly absorbed long wavelength light is prevented from escaping the cell by ensuring reflection at the internal surfaces, has made possible the use of much thinner substrates than was hitherto possible. Light trapping schemes which are based on increasing the path length of light in order to extend the probability for absorption. Light trapping is typically implemented by providing a reflective rear surface, by roughing or texturing the surfaces [11,12] and by providing reflecting cavity [13] and reflective gratings [14] to increase the possibility of total internal reflection. This occurs in c-Si for all rays incident at angles greater than 16 ～ 17° to the normal. Such schemes are shown [15] to be capable of path length enhancements of up to a factor of 50 in c-Si.

Thin c-Si cells offer the promise of both improved current and voltage performance over traditional thick c-Si cells. Higher currents are possible because photogenerated carriers are produced closer to the collecting junction enhancing the collection efficiency. This enables the use of material of a lower quality, with thus a shorter minority carrier diffusion length, than would be necessary in a thick cell with a comparable collection efficiency. Increased voltages are possible because the reduction in cell volume results in reduced recombination of photogenerated carriers relative to a thick cell of comparable crystal quality. This reduced recombination volume leads to a smaller saturation current and thus a higher open circuit voltage.

Various approaches [16] have been investigated for the fabrication of thin c-Si substrates. As the thin Si films require transparent material in direct contact with both sides of the Si absorber to trap light effectively polycrystalline films should be grown on non-Si substrate. Foreign substrates has to meet a number of requirements: low cost, good chemical and mechanical stability, good thermal expansion match with silicon and low contamination levels. MG (metallurgical grade) Si [17], stainless steel [18], graphite [19] and specially prepared ceramics [20] have been considered as substrates for thin film Si solar cell.

Liquid phase epitaxy (LPE) involves the epitaxial deposition of c-Si from a saturated metal solution. LPE has proved itself capable of producing material superior to that produced by other methods and offers the advantages of low growth temperature, large grain growth, and long minority carrier diffusion lengths. Barnett et al. have demonstrated large-grained (＞100 μm) continuous polycrystalline silicon thin films on steel, quartz and ceramic substrates from tin solutions at temperatures around 900 ℃

[21]. Conversion efficiencies of 10.9 % and 14.9 % have been reported, respectively, for a 100 cm^2 commercial size cell and a 1 cm^2 laboratory cell based on this approach [20]. An LPE project is underway at UNSW with the emphasis on low temperature solutions, facilitating ease of processing, and an investigation of novel sub/superstrates. The 'ultimate' cell configuration envisaged would see the deposition of c-Si onto a glass superstrate removing some of the division between cell and module fabrication, thus still further reducing costs.

In thin-film approaches, much of the device fabrication will undoubtedly take place during layer deposition by controlling the dopant type concentration. The ability to deposit multiple layers of opposite polarity in a single processing step opens up enormous flexibility for device structures. It may well be that multiple interleaved n-type and p-type layers each with a thickness comparable to the respective minority carrier diffusion lengths, may have particular advantages with regard to performance. Green (UNSW) reported polycrystal cell efficiency of 15.2 % using advanced, buried contact structures [22]. Figure 1 shows a schematic representation of the multilayer cell which consists of multiple, horizontal, interleaved p and n-type silicon layers. Electrical contact is made to all the horizontal layers using the patented Buried Contact approach. The attraction of this multilayer approach is that it allows very low quality material and the use of less silicon to be used to produce high performance devices. By select-
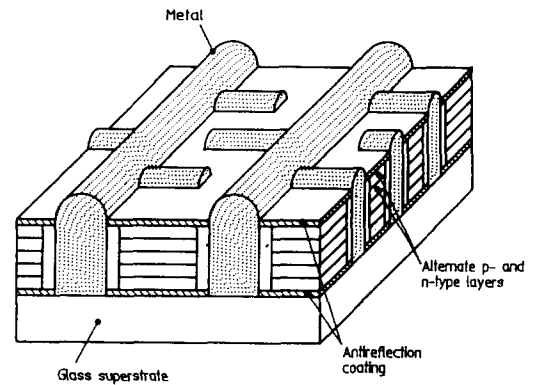

Fig. 1. Schematic diagram of multilayer cell.

ing the thickness of each layer so that it is less than a diffusion length in the cell material, complete collection of photogenerated carriers can be guaranteed regardless of material quality.

3. Thin film a-Si solar cells

For the past several years, since the first a-Si solar cell was reported by Carlson and Wronski in 1976 [23], there has been a great deal of progress in improving the efficiency of a-Si device. The technology of a-Si solar cells fabricated by the glow discharge process promises low cost fabrication of large area solar arrays on inexpensive substrates on an in-line continuous basis [24]. Theoretical estimates place the maximum possible conversion efficiency of a-Si solar cells at 15 % [25,26]. Although efficiencies of 13 ~ 15 % have been predicted and 11 ~ 12 % achieved [27-29], the stabilized conversion efficiency of commercial a-Si PV modules is typically only in the range

of 4~5 %. This degradation is a result of additional defect creation in a-Si : H upon light excitation, phenomena known as Staebler-Wronski effect [30] which has not been solved completely. Recently, impressive progress in stabilized device efficiencies has been made in multi-junction devices at a few laboratories [31,32]. Multi-junction structures, in two and three junction configurations, not only display higher efficiency but an improvement in stability because of thinner layers [33]. Very impressive results in the 13 ~ 16 % efficiency range have lent confidence to the multi-junction approach for obtaining high performance with these thin films. However the best high performance multi-junction devices still have more than 10 % performance degradation upon light soaking [34].

4. Cadmium telluride (CdTe)

Advantageous properties of compound semiconductor used in solar cell are high absorption coefficient, electrically inactive defects, low surface recombination velocity, high quality material at low deposition temperature, various deposition process, variable band gap of alloys and improving property when it reacts with oxygen.

Cadmium telluride (CdTe) is a promising candidate for a terrestrial solar cell due to beneficial properties such as : simple binary phase diagram, congruent evaporation of the compound easy to obtain stoichiometric material, direct energy band gap at 1.45 eV,

doping p and n-type possible, sufficient minority carrier life time and low grain boundary recombination. Because of the short optical absorption length in CdTe and the difficulty of forming a shallow junction with a high conductivity surface layer, thin film CdTe solar cells are of heterojunction type [35,36]. Cadmium sulfide with a direct band gap of 2.43 eV, is a suitable window material for the CdS/CdTe heterojunction solar cell, and a variety of methods, such as hot wall vacuum evaporation [37], screen printing/sintering [38, 39], electrodeposition [40, 41], spray pyrolysis [42,43], chemical vapor deposition [44], close-spaced sublimation [45] and writing [46], has been used to deposite polycrystalline CdS/CdTe films. CdTe is a self compensating material and the role of impurities is still unknown. Thus, obtaining good, reproducible, and optimum doping of CdTe is a research issue for the various deposition technique. The theoretical efficiency of CdS/CdTe solar cell is 27 % [47]. Analysis of manufacturing costs of such modules indicates costs of less than $ 3/Watt. Among the polycrystalline thin film technologies based on CIS, CdTe and silicon film, only CdTe cells are commercially available [48].

Efficiencies over 10 % have been achieved with all polycrystalline CdS/CdTe solar cells. The structure of CdTe thin film photovoltaic cell is shown in Fig. 2. Thickness of most of the CdTe solar cells ranges between 2 to 5 μm with the exception of screen printed cells (15 ~ 30 μm). One of the key technology issues for CdTe is the contact stability. Ohmic
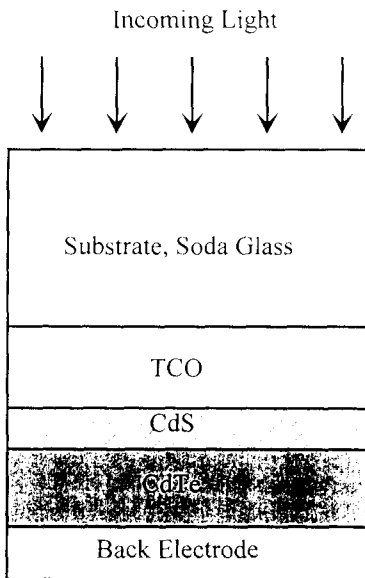
Incoming Light

Fig. 2. CdTe thin-film photovoltaic cell structure.

contacts for CdTe are not very stable and quite sensitive to moisture and air. Ametek circumvented this problem by sandwiching undoped CdTe film between n-CdS and p-ZnTe [49,50]. IEC (Institute of Energy Conversion) has also concluded that the ZnTe : Cu contacts in an n-i-p structure are the more stable than either Au or Cu-Au contacts. Ikegami reported that efficiency of sintered CdS/CdTe solar cell increased by adding $50 \sim 100$ ppm $CuCl_2$ into the carbon contact due to a decrease in contact resistance which was probably caused by the formation of p^+-CdTe layer in the vicinity of the carbon contact during annealing [51]. Another critical issue hindering the CdTe technology is public's perception about the use of cadmium. A possible solution is a very careful development of manufacturing and

recycling process. Patterson reported that module fabrication process would have little effect on the workforce and the environment and the environmental impact from product use or as a result of a storage fire would also be very low [52].

5. Copper indium diselenide ($CuInSe_2$)

$CuInSe_2$ and the related chalcopyrite compounds are direct semiconductors and thus have a high optical absorption coefficient exceeding 4×10^4/cm even near the bandgap. Among this group, $CuInSe_2$ is the most promising material. Interest in thin film $CuInSe_2$ solar cells was raised by the successful demonstration of high efficiency heterojunction photovoltaic device on a single crystal of this material in 1974 [53]. The major reason for this popularity is the efficiency improvements in recent years and the remarkable stability shown by the $CuInSe_2$ solar cells and modules [54]. Thin film CdS/$CuInSe_2$ cells have been prepared by various technique such as vacuum flash evaporation [55], spray pyrolysis [56], sputtering [57], and selenization of elemental Cu/In thin films [58,59]. Among these techniques, solar cells with conversion efficiencies near or over 10 % have been fabricated on the $CuInSe_2$ films prepared by the elemental coevaporation technique and by two-stage process [60,61]. The structure of the solar cell is somewhat complex as indicated in the cross-sectional representations of Fig. 3. [62,63]. In the figure high resistivity CdS
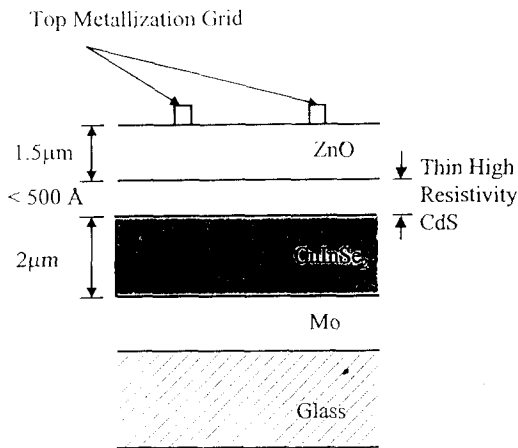
Top Metallization Grid

1.5μm

ZnO

< 500 Å

↓ Thin High
Resistivity

⊤ CdS

2μm

CuInSe₂

Mo

Glass

Fig. 3. CuInSe₂ solar cell cross section.

and CuInSe₂ near the junction were used to prevent copper cones or precipitates from forming at the hetero-interfaces of the three source produced cell, destroying the junction properties [64]. CIS cells have achieved efficiencies in excess of 12 % and recently demonstrated module efficiencies of 11.2 % with no apparent instabilities. This, and the fortuitous near ideal band gap difference, has lead to the idea of combining them into a four-terminal tandem structure in an attempt to obtain higher efficiencies. This structure involves the use of a thin semi-transparent a-Si top cell under which is mounted and electrically isolated, but optically coupled CIS cell. The bandgap difference between the two alloys sufficient long wavelength light to be coupled into the underlying CIS cell to bring the combined module efficiency towards the 15 % mark. This approach has lead to 15.6 % cell efficiencies and 12.3 % module efficiencies (Prior to a-Si degradation). Much of today's research is centered

on the use of alloys, either by substituting sulfur for selenium or gallium for indium, which allow the synthesis of a full range of band gaps. ARCO Solar, Inc., the worlds largest PV manufacturer, who have been developing this tandem approach were so impressed, though, with their recently achieved CIS module efficiency, that is may proceed with commercialization of this technology without necessarily pairing it in tandem module. Costs for these technologies are hard to gauge though the $ 1/Watt manufacturing cost for volume production (MW +) often quoted by the industry as an aim for a-Si can be taken as an indicator. The technical issues about the CIS are the control of stoichiometric and uniform deposition of CIS film that determine the performance of CIS solar cells. Issues with the glass substrate (dirt, imperfection) and the back contact (Mo berms, adhesion) for CIS have been cited as central to delays in introducing CIS product. Table 1 represents confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m²) [65].

6. Conclusions

This paper discussed the status of the thin film photovoltaics. The high production costs of thick high-efficiency crystalline Si solar cells are inhibiting wide spread application of photovoltaic devices.

The rapid advances in performance demonstrated by the newly emerging thin film c-

Table 1

Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m^2)

Classification	Efficiency (%)	Area (cm^2)	Description
Si (large thin film)	14.2 %	100	Mitsubishi
a - Si (cell)	12.7 %	1.0	Sanyo
a - Si (submodule)	12 %	100	Sanyo Unstabilized result
CdTe (cell)	15.8 %	1.05	South Florida CSVT
CdTe (submodule)	9.8 %	63.6	Solar Cell Inc.
CIGS (cell)	13.9 %	6.636	NREL
Cu (In,Ga) (S,Se) (submodule)	12.7 %	69.1	Siemens
a - Si/CIGS	14.6 %	2.4	ARCO(4 - terminal) Unstabilized result

Si technology, coupled with the promise of performance levels comparable with established c - Si technology makes this a most promising candidate for a PV power technology of the 1990's.

Although industry worldwide continues to invest heavily in a - Si it is difficult to conceive of this material breaking from the consumer electronics to the power market without a resolution of the Staebler - Wronski degradation effect.

Progress in developing CuInSe$_2$, CdTe and Si - films continues to be very strong. Such progress should continue, since cell efficiencies are still rising, and the ultimate practical efficiencies of these material are 16 ~ 18 %.

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