Current Situation of Amorphous-Si Technology for Solar Cells

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1. Advantages of amorphous silicon

Hydrogenated amorphous silicon (a-Si) has been investigated for a promising and potential material for low cost photovoltaic devices. A-Si has the following advantages:

1) It consists in a thin film

A-Si has a greater absorption coefficient than monocrystalline Si in the visible light region; the film thickness required for photo-electric conversion is as little as 1 μm and the quantity of Si required per watt is extremely small.

2) Energy pay-back time is short

The electric power required for the manufacture of a-Si solar cells is less at every state than that for monocrystalline Si solar cells. The time taken to cover the cost of the electric power needed for manufacture with the electric power obtained from the solar cells themselves is called the 'energy pay-back time'. With conventional monocrystalline Si this is 10-15 years; even with improved Si solar cells, energy-saving by computer control and advanced automation methods, it takes 3-5 years. With a-Si it takes barely a year.

3) It can be formed on any substrate

A-Si can be formed on any substrate, whether it be vitreous or metallic. If, for example, glass is used as the substrate, this can be used, without modification, as the glass cover for the module.

4) Continuous production is easy

Compared to the manufacture of monocrystalline and polycrustalline Si solar cells, a-Si involves fewer processes and offers, therefore, the possibility of continuous production.

2. Device applications of a-Si

In the past decade, a-Si has developed into an important family of semiconductors. In a-Si alloys with germanium, the energy gag decrease with increasing germanium content, while in alloys with increasing carbon content the energy gap increases. The main application of a-Si has been concentrated to solar cells. The a-Si solar cells is now popularly used as electric power source for consumer electronic calculators under fluorescent lamp. The other applications are as follows:

1) Electrophotography

A-Si is endowed with a very low electrical conductivity, a long charge decay time, an excellent spectral sensitivity in the visible, and a good chemical intertness. The rentention of a surface charge is helped by blocking layers at both surfaces of the a-Si films. An excellent image reproducibility with high resolution and good contrast was demonstrated in a commercial machine whose Se-coated drum was replaced by one coated with a-Si.

2) Field-effect transistors (FETs)

Although the development of field-effect transistors (FETs) has already reached a high level of perfection in crystalline silicon, a-Si offers the advantage that very large arrays of a-Si FETs are feasible. Hence, even if their performance level is much lower than that of c-Si FETs, there are still many applications where their characteristics may be adequate.

3) Image sensor

A-Si is more suitable as a photoconductor for this application than other materials because of its flatter response in the visible spectrum and because the fabrication of a long array is readily feasible. It is expected that a superposition of the a-Si sensor and a charge-coupled devices (CCD) should produce a performance comparable to that of a vidicon. With the addition of a laminated color filter comprising lines of red-, green-, and blue-pass filters, a color image sensor was demonstrated.

3. Fabrication technologies of a_si

1) Plasma-CVD(rf glow discharge)

Plasma-CVD method is the most popular for preparing a_si films. With regard to the a-Si solar cell fabrication, the attainment of the conversion efficiency over 11% by plasma-CVD. The conditions for forming a-Si by the plasma-CVD are as follows; The substrate temperature is set a 200-300°C, monosilane and disilane are used

for the reactant gases. The gas pressure is maintained at 0.1-10 torr. When a 13.56 MHz high frenquency voltage is applied, electric discharge is begun, and a-Si accumulates. The best film quality is obtained by the deposition rates of 1-2 A/s.

2) ECR plasma-CVD

Recently, ECR9electron cyclotron resonance) plasma-CVD has attracted special interest as a new technique for deposition of a-Si and its alloys. Hamakawa et al. reported that boron doped a-SiC film prepared by ECR plasma-CVD had a high conductivity and application of this film to the p-layer of a-Si solar cells resulted in improvement of the open-circuit voltage(1). Watanabe et al. applied this technique to forma - tion of a-SiGe films, and obtained highly photo-conductive narrow bandgap films (2). Thus, this technique has a possibility to become a key for improving the conversion efficiency.

3) Photo-CVD

The plasma-CVD method has generally been used in the manufacture of a-Si solar cells. However, it appears that the interfaces and growing films are damaged by the bombardment of ionized particles. The performance of a-Si solar cells prepared by plasma-CVD might be thus less than optimal. An alternate deposition methods, the photo-CVD technique, seems more suitable for damage-free film preparation. This is because the photon energies of the low-pressure mercury lamp used are lower than the ionization energies os silanes and their neutralradicals. The relative absence of ionized radicals in photo-CVD cells leads to interfaces and bulk layers of high quality and should show an improvement over plasma -CVD cells.

4. A-Si films prepared by Photo-CVD

Since Saitoh et al. showed that high-quality a-Si films could be prepared by photo-CVD in 1982(3), continuing research has been directed towards improving film quality and device performance and moving from small-area to module-size depositions. Photo-CVD processes can be divided into mercury-sensitized and direct processes, the latter using either a lower-pressure Hg lamp or a laser as the energy source. In this chapter, a review is given of the current status of a-Si and related alloys prepared by photo-CVD.

1) Mercury-Sensitized Photo-CVD

(1) Undoped a-Si

(a) Mercury phtosensitization

The mercury photosensitization of monosilane and disilane has earlier been investigated in detail by Pollock et al.(4). The primary steps of these processes are the following:

$$Hg^* + SiH_4 \longrightarrow Hg + H + SiH_3$$
$$Hg^* + Si_2H_6 \longrightarrow Hg + H + Si_2H_5,$$
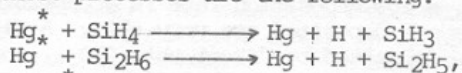
where Hg^* indicates the excited state of a mercury atom due to UV irradiation. Hg-photosensi_

tization of monosilane using the 254nm and 185nm wavelenths is highly selective and yields,almost exclusively, SiH_3 radicals.

(b) Photo-CVD apparatus

Figure 1 shows a separate-chamber photo-CVD system developed by the author. It consists of four reaction chambers and one loading chamber partioned by gate valves. Undoped films are prepared in the i-a-Si chamber. A major limita - tion of photo-CVD has been the unintended deposition of silicon on the UV transparent quartz window of the reaction chamber. We have found that coating the quartz window with perfluoro polyether is useful in preventing the window getting "clouded". As a result, the deposition thickness is linear with time up to a thickness of 3 μm. Typical deposition rates are 1-3A/s for both monosilane and disilane.

Two novel techniques for keeping the window transparent have been developed. Rocheleau et al. devised a new photo-CVD reactor with a mobable UV-transparent Teflon film (PFA, 1mil) and secondary gas flows to eliminate window fouling(5). In the second technique, developed by Langford et al., an etchant compatible with the normal film deposition process (XeF_2) is used to maintain window transparency(6).

(c) Film properties

Figure 2 shows the variation of dark and photoconductivities and the deposition rate as a function of the gas pressure for monosilane-based a-Si films. The photoconductivity (measured under AM1, 100mW/cm^2 insolation) differed from the dark conductivity by a factor of over 10^6. The maximum photo/ dark ratio is 5x10^6. We have also evaluated the density of states(DOS) at midgap by the space-charge-limited current method proposed by Solomon et al. (7). The calculation showed a gap states density of around 5x10^{15}/cm^3 eV for our samples. These results suggest that the quality of the undoped a-Si films produced by photo-CVD is reasonably good.

Tarui et al.(8) have investigated high-rate deposition processes for a-Si films using mercury-sensitized photo-CVD. They found that the deposition rate depends on reactant gas pressure, light intensity, and the concentration of mercury atoms. A maximum rate of 100 nm/min was attained by optimizing the deposition conditions.

(d) Residual impurities

In a-Si solar cells, the reduction of impurities in undoped layers is one of the key methods to improve cell performance and to eliminate the Staebler-Wronski effect.

Impurity concentrations in a-Si films fabricated by a single chamber(without a loading chamber) and a separate chamber, measured by IAM, are shown in Fig. 3. In Fig. 3, the impurity

concentrations in plasma-CVD a-Si films reported by kuwano et al.(9) are also included. In photo-CVD samples, we observed a drastic reduction of impurity levels such as O,C, and N when separate chambers were used. The absolute impurity level in photo-CVD a-Si films is very similar to that of separate chamber plasma-CVD a-Si films, but is one order higher than that of super-chamber plasma-CVD a-Si films.

Rocheleau et al. also reported the effect of atmospheric contaminants on the properties of a-Si films and on cell performance(10). The C,O, and N impurity concentrations have been well with the residual gas levels in the reactor. The mid-gap DOS was reduced to $2x10^{15}$ /cm eV in the sample with the lower carbon and oxygen concentrations.

(2) A-SiGe

A reason for using the photo-CVD process in a SiGe films is that it makes it possible to control hydrogen radicals(11). In the prelinary stage of development, we found that the phtoconductivities of a-SiGe films decreased rapidly with increasing Ge content if no hydrogen was introduced. The reduction in the photo-conductivity is similar to that of convencional glow discharge films. In this case, it is strongly related to an increase in the number of Ge dangling bonds due to the weakness of Ge-H bonds. In order to reduce the densities of dangling bonds, we examined the effect of hydrogen radicals on electrical properties. The photo-conductivity improved drastically as the gas ratio was raised.

The film properties of recently developed a-SiGe fabricated by various methods as shown in Fig. 4. Phtoconductivities of a-SiGe films prepared by a triode plasma-CVD, ECR and photo-CVD are nearly the same and gradually decrease from about 10^{-4} S/cm as the optical bandgaps decrease.

Tsuda et al. have prepared a-SiGe:H:F using GeF_4(12). They concluded that specially in the case of using fluorinated gases, the photo-CVD method is a promising way to remove the damage of high-energy fluorinated radicals existing in GD plasma-CVD.

(3) Microcrystalline Si

Undoped and doped hydrogenated amorphous-microcrystalline mixed-phase(μc-Si) filmes have been prepared by mercury-sensitized photo-CVD of a mixture of silanes and hydrogen gas. It was found that the hydrogen radicals plays a significant role in the formation of μc-Si. P-type and n-type μc-Si filmes are specially promising materials for solar cell applications.

The preferencial orientation of the crystal-lites was found to be more pronounced in photo-CVD films than in films deposited by the conventional GD method. The crystallites in the film were mainly oriented in the <110> directions.The maximum dark conductivity and optical bandgap of the n-type μc-films obtained were 80 S/cm and 1.9 eV, respectively. A maximum conductivity of about 1 S/cm was obtained for p-type μc-Si.

2) Direct Photo-CVD

(1) Undoped a-Si

(a) Lamp process

Mishima et al. reported on the first trial of a-Si film formation by direct photolysis of disilane at atmospheric pressure using a low-pressure Hg lamp in 1983(13). However, the depo-sition rate was low (15A/min). Kumata et al. reported that the deposition rate of a-Si films prepared from Si_3H_8 by the direct photo-CVD was five times that using Si_2H_6(14). The conductivity of the film prepared from Si_3H_8 at 300 C was 10^{10} S/cm in the dark and 10^{-5} S/cm with He-Ne laser at a photon flux of 10^{-15}/cm^{2}s. High-rate deposi-tion of a-Si films could also be achieved by direct photo-CVD using emission peaks from deuterium(D_2) and Xe discharge lamps whose wavelengths (D_2:160.8nm, Xe:147 nm) were much shorter than the absorption edge of Si_2H_6 (187 nm). The maximum deposition rate reported, 75 A/min, was obtained by Fuyuki et al.(15).

(b) Laser induced photo-CVD

To enhance the deposition rate of a a-Si films, ArF(193nm) excimer laser induced CVD (LCVD) has been demonstraded using monosilane (two-photon process) and disilane(16,17). In our configuration, the laser beam was parallel to the substrate, thus avoiding substrate heating effects. Amorphous Si films were rapidly deposited(559/s) by using disilane. But the films prepared at a high deposition rate incorporated more hydrogen; the Si and H bond structure of the films changed from monohydride to dihydride, and these hydrogen atoms might generate defects.

A dark conductivity of $2x10^{-9}$ S/cm and a photoconductivity of $2x10^{-4}$ S/cm were obtained at a substrate temperature of 400ºC and a deposi-tion rate of 1A/s(17). These electrical properties are somewhat inferior to those of films deposited by conventional plasma-CVD and photo-CVD(lamp process). The high values of the photoconductivity were observed either at a high substrate temperature or at a low deposition rate.

(2) P-type a-SiC

The UV-lamp direct photo-CVD process is now being investigated to preparate p-type SiC for the solar cell window material. In this kind of application, a low deposition rate is acceptable since the layers deposited are very thin. A-SiC films can be deposited by direct phto-CVD of mixtures of disilane and methylsilanes or

acetylen. GD-plasma a-SiC films and photo-CVD films were compared by the author(18), through the optical bandgap, conductivities and activa - tion energies measured as a function of the boron doping concentration. Photo-CVD p-type a-SiC films showed about one order of magnitude higher conductivities and about 0.1eV lower acti vation energies than the GD-plasma films. High conductivities (2.2×10^{-5} S/cm) and low activation energies (0.29 eV) were abtained at an optical bandgap of 2.0 eV by the author's group.

Ichimura et al. have also reported on photo-CVD p-type a-SiC films having high conductivity compared with GD films at optical bandgap of 1.9 - 2.1 eV(19). They found that the carbon content for the photo-CVD film was lower than that for the GD film. This suggests that carbon in the photo-CVD film is indorporated more effectively into the silicon network. These data support the view that the photochemically prepared a-SiC films can be used more effectively as a window layer in a p-i-n a-Si solar cell.

3) Atmospheric-pressure photo-CVD

It has been reported that impurities such as O, N, and C in the i-layer have a strong influence on film properties and the light-induced degradation of a-Si:H solar cells(20). Growth chambers having a high vacuum with a back-ground pressure of 10^{-9} Torr were used for reducing the impurities. However, no remarkable improvement in light-induced degradation has been reported yet.

The trowth of high quality undoped a a-Si films with a high conversion efficiency of 11.2% prepared by low-pressure photo-CVD Si films by atmospheric-pressure mercury sensitized photo-CVD in order to reduce the impurities of the undoped films further and to obtain higher film quality(22). It is expected that the impurity contamination in the films under atmospheric-pressure conditions is less than that at low-pressure conditions at the same back-ground pressure due to the lower leakage out of the growth chamber.

At first, we tried to prepare a-Si:H films by mercury-sensitized photo-CVD. at the present knowledge, mercury incorporation into the deposited films appears to be negligible. The deposition rate is strongly depended on the temperature of the mercury reservoir, and to date the maximum deposition rate that we have obtained is 45A/min.

The electrical and optical properties of the undoped a-Si films prepared by atmospheric-pressure photo-CVD were investigated. Figure 5 shows the variation of the conductivity and the optical bandgap as a function of the flow rate of SiH4. The substrate temperature was 300°C. No significant change in optical bandgap was found in the range of 5-30 sccm. As for the electrical properties, the photoconductivity was larger than the dark conductivity by over

10^0 in the range of 5-20 sccm, and the maximum $\Delta\sigma_{ph}/\sigma_d$ value was 6×10^6 at a SiH flow rate of 20 sccm, which indicates that the quality of the undoped films is reasonably good. Furthermore, no powder formation was found in the range of SiH4 flow rate of 1-30 sccm.

Figure 6 shows the concentration of oxygen in the films prepared by the low- and atmospheric-pressure photo-CVD methods, respectively. The concentration of oxygen in the films prepared by atmospheric-pressure photo-CVD is much lower than in the films grown by low-pressure photo-CVD. The concentration of oxygen we abtained was 2×10^{18} cm^{-3}. We assumed that the high quality of the undoped a-Si films (over in photosensitivity) is due to the lowered oxygen concentration in the films. Even higher quality films can be expected by, (a)preparing the films using a load-lock system and (b)optimizing the deposition conditions.

5. Typical characteristics of a-Si

The typical characteristicas of a-Si prepared by photo-CVD summarized in Table 1.

6. A-Si single junction solar cells

1) Techniques for rasing efficiency

Nowadays, the term 'amorphous solar cell' generally signifies the p-i-n type. The term 'p-i-n type' covers a number of different structures, however, glass/SnO2/p a-SiC/i/n a-Si/metal solar cells are the most widely used. In this structure, a transparent conducting film (TCO),is deposited on the glass substrate with a CVD process. The TCO material is generally fluorinated SnO2.

The first means of raising efficiency is to decrease the loss of sunlight by surface refle - tion. In order to increase light utilization, the surface of SnO2 film is textured. Texturing should be otimized to reduce the optical reflection of the sunlight and to increase the optical path length in the cell. In addition, a highly refleting rear contact comprised of ITO(Indium Tin Oxide) overcoated with silver is sometimes used to achieve reflectivities close to 100%.

A second means of raising efficiency is to decrease the amount of absorption in the p-layer since absorption there does not contribute to the current generated by the cell. The "window effect" appears promising for this purpose. The standard p-layer consists of a-SiC with an optical bandgap of 2.0 eV doped with boron and is typically 100-150 Å. The carbon is incorporated to increase the bandgap, but a-SiC of Eopt higher than 2.0 eV has a high resistivity, which is a factor tending to lower the fill factor. The glow discharge CVD method has generally been used in the manufacture of a-Si solar cells. However, several new techniques have recently been developed to increase the conductivity of the p-type window layer. One approach is to use photo-CVD. The other approach includes the application of p-type μc-Si

or μc-SiC. Hattori and co-workers (1987) reported that highly conductive p_type μc-SiC films could be prepared by ECR (Electron Cyclotron Resonance) CVD. Their material, which has an optical bandgap of 2.25 eV, exhibits a dark conductivity as high as 10 S/cm which is more than seven orders of magnitude higher than that of material prepared by conventional glow discharge CVD. A remarkable increase in the open-circuit voltage to 0.965 V has been obtained with a conversion efficiency of 11.8% so far.

The third means of raising efficiency is to ensure that the carriers obtained by excitation in the i-layer are efficiently conducted to the external circuit. The most important point in raising the efficiency of carrier collection is to improve the quality of the i-layer. Localized states in the bandgap act as recombination centers which limit the collection of carriers, so these states need to be minimized. The lowest values obtained for the density of states near the middle of the bandgap with glow discharge CVD, the standard, method used by the industry today, is about $5 \times 10^{15}/cm^3$ eV. Recently, atmospheric-pressure photo-CVD has been examined to prepare high quality undoped a-Si films. It is expected that the impurity contamination in the films under atmospheric-pressure conditions is less than that at low-pressure conditions at the same back-ground pressure due to the leakage out of the growth chamber.

A-Sic has been widely used for making p-layer material. However, solar cells incorporating such layers may have a large number of defects near the p(a-SiC)/i(a-Si) heterointerface. It is becoming clear that the p/i interface plays an important role in determining the performance of a-Si solar cells. One method to reduce interface recombination involves the creation of a "buffer" layer, i.e. by grading the bandgap the p/i interface to retard electron back diffusion to the contact. Solar cells with a buffer layer have markedly higher open-circuit voltage and short-circuit current than cells without the buffer layer (21).

2) Achievable efficiency

The author's group has developed a detailed and comprehensive computer simulation model for a-Si p-i-n solar cells. The novel feature of this model is that its quantitative treatment of the interfaces in the cells makes it possible to study the impact of various interface conditions on the overall performance of the cell. It is evident from the results of the model that the p/i and TCO/p interfaces are critical to cell performance. If the improvement of the p/i and TCO/p interfaces is combined with the use of a high quality i-layer, our calculations indicate that it would be possible to raise the conversion efficiency of p-i-n a-Si solar cells to about 15%.

7. Problems in a-Si single junction solar cells

A-Si solar cell have the intrinsic possibility of reduction of the amount of silicon material, the very low energy consumption during manufacture, the small number of processes and the continuous automatic processability. However, despite the expected possibility of substantial cost reduction, several technological barriers remain for a-Si solar cells such as lack of knowledge in film deposition chemistry and physics and light-induced performance degradation, and the inferiority to crystalline silicon solar cells in conversion efficiency and long-term reliability.

In order to raise conversion efficiency and to deduce light induced-degradation, Tandem type solar cell is the most useful candidate. High efficiency can be attained in principle by utilizing tandem solar cells consisting of a combination of solar cells of materials having different bandgaps, because the various layers collect photons of different wavelengths efficiently. Furthermore, the light-induced degradation can be quite reduced in the tandem solar cells than the single junction solar cells.

8. Prospects for the future

As the technology matures, the progess inevitably slows. This is particularly evident in the single junction devices where no substantial increases in performance have occured recently. A similar observation can be made for alternate amorphous materials, such as a-SiGe and for hybrid pairs such as $CuInSe_2$. Fortunately, the larger area modules and submodules are tracking in efficiency with the smaller devices and community should expect continued performance improvements over the next few years. Recent theoretical analysis by computer simulation indicate that over 20% tandem module using a-Si/a-SiGe/CIS is possible. If this configuration can indeed be produced, at reasonable cost, the destiny of thin film photovoltaics will be realized.

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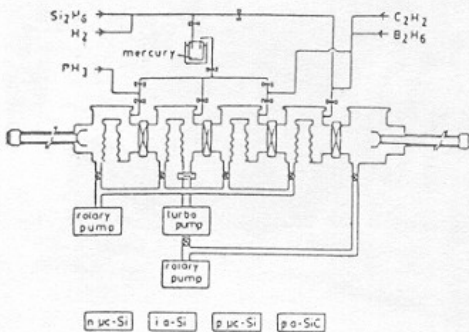
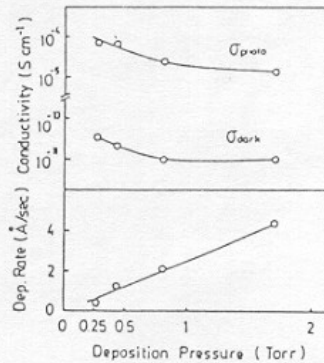Fig.1: Schematic diagram of four-separate-chamber photo-CVD system.

Fig.2: Variation of conductivities and the deposition rate as a function of gas pressure.
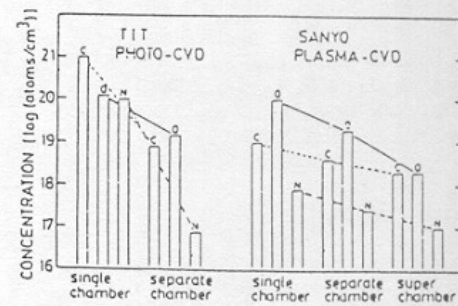

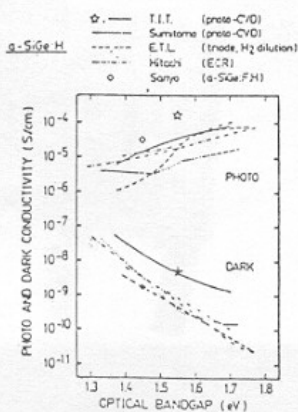Fig.3: Impurity concentration in a-Si films fabricated by photo-CVD and plasma-CVD.

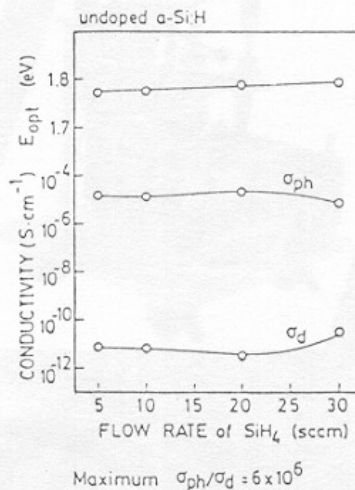Fig.4: Electrical properties of recently developed a-SiGe films fabricated by various methods.

Maximum $\sigma_{ph}/\sigma_d = 6 \times 10^6$

Fig. 5. Variation of the conductivity and the optical bandgap as a function of the flow rate of monosilane.
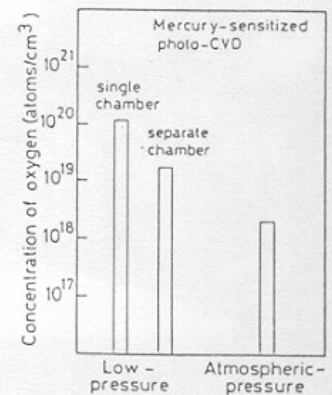

Fig. 6. Concentration of oxygen in the films prepared by low- and atmospheric-pressure photo-CVD.