

Thin-film crystalline silicon solar cells

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A photoelectric conversion efficiency of over 10% has been achieved in thin-film polycrystalline silicon solar cells which consists of a 2 μm thick layer of polycrystalline silicon with a very small grain size (microcrystalline silicon) formed by low-temperature plasma CVD. This has shown that if the recombination velocity at grain boundaries can be made very small, then it is not necessarily important to increase the size of the crystal grains, and that an adequate current can be extracted even from a thin film due to the light trapping effect of silicon with a low absorption coefficient. As a result, this technology may eventually lead to the development of low-cost solar cells. Also, an initial efficiency as high as 12% has been achieved with a tandem solar cell module of microcrystalline silicon and amorphous silicon, which has now started to be produced commercially. An even greater initial efficiency of 14.5% has been achieved in devices with a small size area, and further increases of efficiency can be expected.

Keywords: solar cell, silicon, light trapping, thin film, microcrystalline, plasma chemical vapor deposition, recombination velocity

1. Introduction

With raw materials for crystalline solar cells in increasingly short supply, renewed efforts are being made in the study of ways to make practical thin-film solar cells for use in tomorrow's large-scale solar cell installations. In particular, since thin-film polycrystalline silicon solar cells are made of the same materials as bulk silicon solar cells which are currently in widespread use, they are being enthusiastically studied at laboratories all over the world due to the abundance of raw materials for such devices, their stability, and the characteristics they are expected to possess as silicon devices. Part of the motivation behind these

studies comes from the theoretical finding that if these devices can be constructed so that they trap sufficient light, it should ideally be possible to achieve photoelectric conversion efficiencies in excess of 20%, even with solar cells in which the photoelectric layer is just a few μm thick.¹⁾

Historically, the silicon thin-film photo absorbed layers in such devices have been produced by high-temperature processes, mainly chemical vapor deposition (CVD),²⁾ liquid phase epitaxy (LPE),³⁾ and zone melt recrystallization (ZMR).⁴⁾

However, it has become apparent that the properties of the underlying substrate are the key to obtaining high-performance silicon thin-film solar cells. That is, a high-quality silicon thin-film photoelectric layer can be obtained by suppressing the diffusion of impurities from below and using epitaxial deposition that exploits the characteristics of the underlying material, and evidently single-

crystal silicon has become the optimal material for the substrate. Accordingly, this research has shifted toward recycling single-crystal silicon, and at present research is being actively performed into single-crystal silicon thin-film solar cells, primarily focusing on porous silicon delamination techniques.⁵⁾

On the other hand, attention has recently been focused on thin-film solar cells made with crystalline silicon having a small grain size formed by plasma CVD using inexpensive substrate materials such as glass and by using low temperatures regardless of the type of substrate instead of these high-temperature processes.⁶⁻¹¹⁾

Figure 1 shows the relationship between grain size and V_{oc} (open circuit voltage) as summarized by J. Werner of Stuttgart University.¹²⁾ Here, V_{oc} can be regarded as a parameter reflecting the cell characteristics and crystalline properties. As the figure shows, superior characteristics are obtained with a

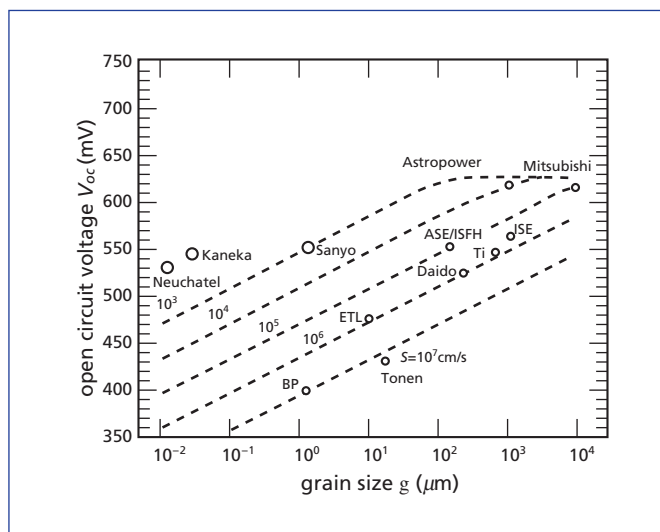


Fig. 1: The relationship between grain size and open circuit voltage (V_{oc}) in solar cells. V_{oc} is correlated to the carrier lifetime (diffusion length). In the figure, S indicates the recombination velocity at the grain boundaries. In this paper, microcrystalline silicon cells correspond to a grain size of 0.1 μm or less. In the figure, Ti, BP, ASE and ISE are abbreviations of the research facilities from which the associated data came.

grain size of 100 μm , but the characteristics are worse with a grain size of a few tens of μm . Conversely, favorable characteristics have been obtained experimentally both at Neuchâtel University and at Kaneka Corporation's PV Research Division by using thin-film polycrystalline silicon formed at low temperatures by plasma CVD with a submicron grain size (this is generally referred to as microcrystalline silicon due to the small grain size). This is an interesting discovery which has caused recent research to shift toward both extremes.

This report discusses these thin-film polycrystalline silicon solar cells formed at low temperature (referred to as microcrystalline silicon solar cells below) which have been the subject of studies conducted by the PV Research Division using thin-film polycrystalline silicon with a very small grain size formed at low temperature. It will also introduce the results of the research and development of silicon hybrid solar cells with a tandem structure comprising these solar cells and amorphous solar cells, which were put to practical use for the first time in 2001.

2. Thin-Film Polycrystalline (Microcrystalline) Silicon Solar Cells

2.1 Microcrystalline silicon thin-film solar cells formed at low temperature

Microcrystalline silicon solar cells formed by plasma CVD at low temperature are assumed to have a shorter lifetime than single-crystal cells, and it is common to employ a $p-i-n$ structure including an internal electric field in the same way as an amorphous solar cell. A $p-i-n$ type microcrystalline silicon solar cell is formed by a process fairly similar to that of an amorphous solar cell. Strictly speaking, these cells can be divided into $p-i-n$ and $n-i-p$ types according to the film deposition order, although the window layer of the solar cell is the p -type layer in both cases.

The characteristics of a cell having a $p-i-n$ structure were first reported by Neuchâtel University.^{6,7)} Unlike an amorphous solar cell, this cell does not deteriorate when exposed

to light. The very first reports on the characteristics of an $n-i-p$ cell were made by the PV Research Division using the light trapping structure described below. These cells had an intrinsic conversion efficiency of 10.7% and an apparent efficiency of 10.1% for a film thickness of 2 μm (surface area 1 cm^2 , measured by the JQA (Japan Quality Assurance Organization)) (Fig. 2).⁸⁻¹¹⁾ Also, by subjecting the silicon film in the photoelectric layer of this cell to XRD (x-ray diffraction) measurements, it was found to have a preferential (110) orientation. The $p-i-n$ and $n-i-p$ cells have different characteristics due to their different fabrication sequences. A large difference is that the underlying layer of a $p-i-n$ cell is the transparent p -type electrode, whereas the underlying layer of a $n-i-p$ cell is the n -type back electrode.

As a general rule, transparent electrodes are made of oxides, and since there is a risk of these oxides being reduced by the hydrogen atoms that are needed to form microcrystalline cells, there is a smaller process window in the cell formation conditions for the $p-i-n$ type. From the viewpoint of the

ease with which integrated structures can be formed, which is a characteristic of thin-film solar cells, an advantage of $p-i-n$ cells is that they can be formed as super straight modules using integration techniques similar to those used for amorphous silicon as described below. On the other hand, it should be possible to make integrated structures of $n-i-p$ cells by methods equivalent to those used for Cu(InGa)Se₂-based solar cells.¹³⁾ At the present time it is difficult to determine which is better, but it should become possible to arrive at a conclusion in terms of cost, performance and applications through the production of sub-modules in the future.

2.2 Carrier transport in microcrystalline silicon thin-film solar cells

To improve the efficiency of these solar cells in the future, it is absolutely essential to gain some understanding of the relationship between the crystalline microstructure including grain boundaries and the carrier transport process, in particular the carrier lifetime (diffusion length) that determines the solar cell characteristics and the recombination velocity

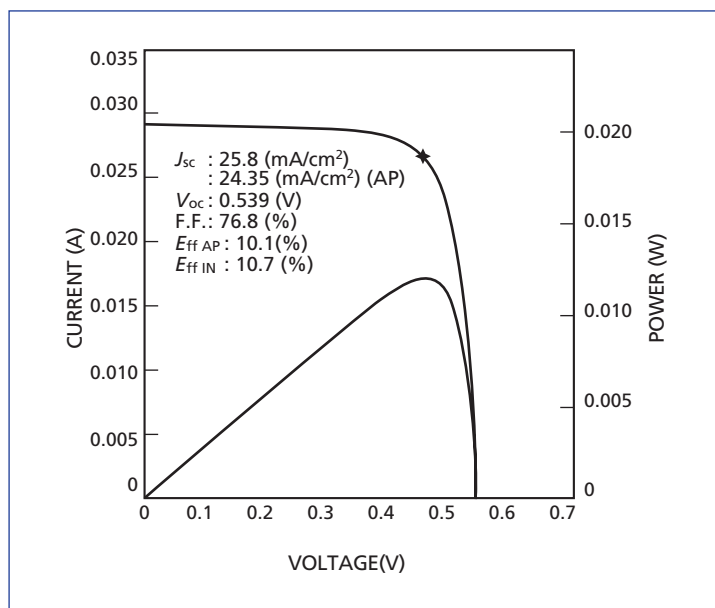


Fig. 2: Current-voltage characteristics of an $n-i-p$ type microcrystalline silicon cell (film thickness 2 μm , area 1 cm^2 , measured by JQA). In this figure, Eff_{AP} is the characteristic for the area including the grid electrode, and Eff_{IN} is the characteristic of the effective area not including the grid.

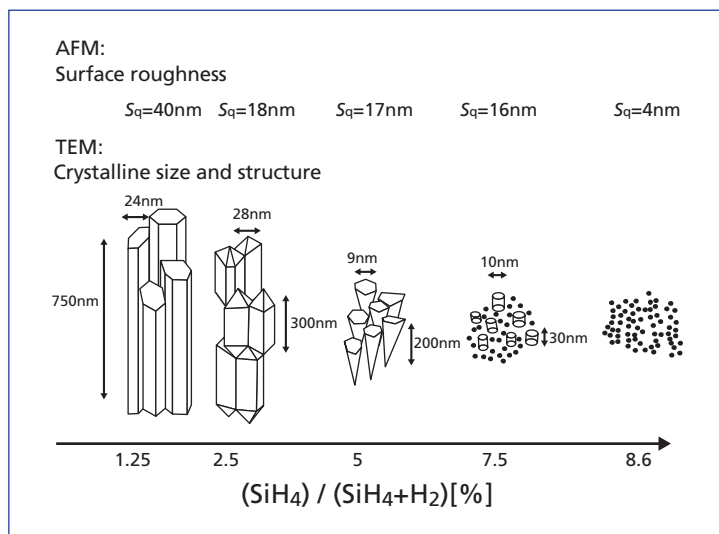


Fig. 3: The variation of crystalline structures in microcrystalline silicon as a function of SiH_4 gas concentration according to the results of measurements by TEM (transmission electron microscopy) and AFM (atomic force microscopy). The small black dots represent the amorphous state. S_q represents the surface roughness (r.m.s. roughness).

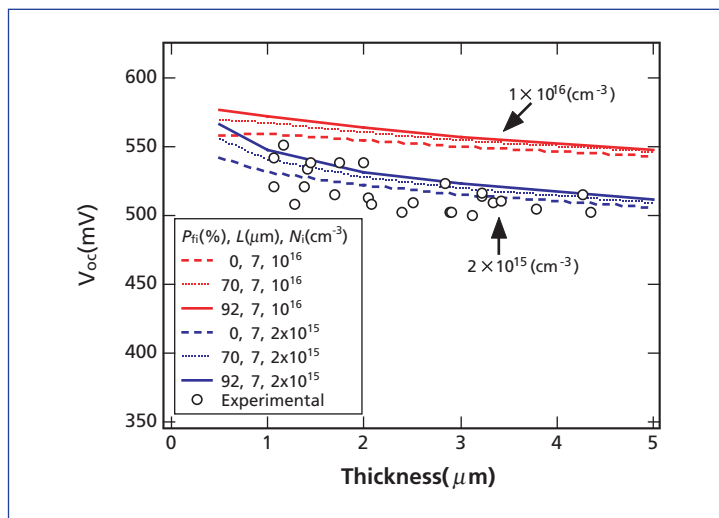


Fig. 4: The variation of V_{oc} with film thickness. In this figure, the open circles represent experimental data, $P_{fi}(\%)$ represents the confinement factor (0%, 70% or 92%), L represents the diffusion length, and N_i represents the carrier concentration. A simulation was also performed using PCID.¹⁰⁾ The simulated results agree well with the experimental data at a carrier concentration of $10^{15}/\text{cm}^3$.

at grain boundaries. However, in a microcrystalline silicon cell, the general non-uniformity that is typical of its grain structure has a direct and complex effect on carrier transport, and thus there have been no conclusive reports relating to these physical properties by direct measurement and analysis. Rather, the efficiency of these solar cells has only recently come to light, so only the first steps have been made in the research of their funda-

mental properties.

A report by Werner et al.¹²⁾ discussed why the very small crystals produced at low temperature (as discussed in the introduction) exhibit relatively favorable cell characteristics. Although the cell characteristics are the product of current, voltage and fill factor, the open circuit voltage (V_{oc}) is directly related to the cell's lifetime and is used here as a guide to the overall cell characteristics. This is be-

cause the current is related to light trapping effects and the cell film thickness as discussed below.

According to Werner et al., the reason why a microcrystalline silicon cell exhibits a characteristic of 10% or more regardless of its small grain size is because of the very low recombination speed at its grain boundaries. This low recombination velocities originates from the small barrier height at the grain boundaries, which is guaranteed by a) the passivation of hydrogen at grain boundary defects, b) uncharged intrinsic grains (low oxygen density), and c) the (110) orientation of the crystal grains.

In Fig. 1, as can be seen from the relationship between the open circuit voltage (V_{oc}), the grain size and the recombination velocities already summarized by Werner et al., further improvement of the lifetime of the crystalline silicon layer (i.e., improvement of V_{oc}) in order to make substantial efficiency improvements may require not only a substantially larger grain size but also a lower recombination velocities at the grain boundaries (e.g., 100 cm/s). Or to put it another way, however much the grain size is increased as shown in Fig. 1, the conversion efficiency decreases when the recombination velocity at the grain boundaries increases (corresponding to a film produced at high temperature).

The actual crystalline structure of a microcrystalline silicon solar cells has been investigated by TEM (transmission electron microscopy) and AFM (atomic force microscopy). For example, Meier et al. at Neuchâtel University have classified the crystalline structures as shown in Fig. 3. Of course the microstructures differ depending on the production process and conditions. It has also been reported that diffusion transport mechanisms are dominant within the grains whereas drift transport is more prominent at the grain boundaries.¹⁴⁾ These grain boundaries exhibit amorphous characteristics which give rise to a passivation effect, and it has been pointed out that this may reduce the boundary recombination velocities.

At the Julich Research Laboratory, Rech et al. evaluated the cell characteristics as a function of the silane concentration with respect to the hydrogen dilution,¹⁵⁾ and showed that

the peak cell performance (where the maximum value of V_{oc} is achieved for the crystal) occurs at the boundary where the resulting film changes from amorphous to crystalline. It is hoped that a more precise analysis of the microstructure and a deeper understanding of its relationship with the boundary recombination velocities will be possible in the future.

To understand the phenomena behind carrier transport, the PV Research Division is at the initial stages of a study into the relationship between V_{oc} and film thickness.^{10,11)}

Figure 4 shows the dependence of V_{oc} on film thickness for a microcrystalline silicon device we produced. The maximum value of V_{oc} we obtained was about 550 mV. As the film thickness decreases, V_{oc} increases slightly. This is thought to be because as the film thickness decreases, the overall number of defects decreases and V_{oc} increases. We thus obtained a result that agrees with the theory stated at the beginning that V_{oc} improves with a thinner film.

This figure also shows the results of simulation by one-dimensional PCID.¹⁶⁾ For a given carrier lifetime (for the case of diffusion length), V_{oc} can be increased by further increasing the carrier concentration. However, according to Werner's findings, this causes the grain boundaries in microcrystalline layers to become weakly n-type, resulting in a higher recombination velocities. This has the effect of causing V_{oc} to decrease, so it is also essential to control the grain boundaries.

In any case, compared with the V_{oc} of highly efficient single-crystal solar cells (about 700 mV), the V_{oc} of microcrystalline silicon solar cells is at least 20% lower, and the key to improving the cell efficiency is to increase V_{oc} —i.e., to improve their lifetime.

2.3 High-rate fabrication of microcrystalline silicon films

To consider the fabrication rate of microcrystalline silicon films, it is essential to understand the film fabrication mechanisms involved. A detailed description of these mechanisms can be found in a report published by Kondo et al.¹⁷⁾

But based on the large amount of experimental data gained by the PV Research Division, the guidelines for forming high-quality

microcrystalline silicon by plasma CVD are very simple—as long as it is possible to supply a sufficient quantity of hydrogen atoms to the substrate during crystallization without causing any damage (most of it is ion damage), then the film fabrication rate can be improved without deteriorating the cell characteristics. Throughput is another important consideration for mass-production, and it is therefore essential to develop ways of depositing films at high speed over large areas. At the PV Research Division, as stated below, we have devised a technique for fabricating uniform thin films of microcrystalline silicon with high quality at a film deposition rate of 1.1 nm/s on meter-size substrates.

2.4 The light trapping effect of microcrystalline silicon cells

Light-trapping techniques are a way of increasing the performance of microcrystalline solar cells. This is a core technique for cells made from microcrystalline silicon because—unlike amorphous silicon—it is essentially an indirect absorber with a low absorption coefficient. That is, the thickness of the Si film that forms the active layer in a microcrystalline silicon solar cell is just a few μm , so it is not able to absorb enough incident light compared with solar cells using ordinary

crystalline substrates. As a result, it is difficult to obtain a high photoelectric current. Light-trapping technology provides a means of extending the optical path of the incident light inside the solar cell by causing multiple reflections, thereby improving the light absorption in the active layer.

Light trapping can be achieved in two ways: (1) by introducing a highly reflective layer at the back surface to reflect the incident light without absorption loss, and (2) by introducing a textured structure at the back surface of the thin-film Si solar cell. Of course, the carrier lifetime is also important, and it goes without saying that the diffusion length must be at least as long as the film thickness.

At the initial stages, we focused on the light trapping effects of textured structures formed on the silicon surface.⁸⁾ We then improved the solar cell characteristics by reducing the film fabrication temperature (although as the film fabrication temperature decreases, the degree of surface texturing also decreases). A solar cell with a textured surface and a back reflective layer for increasing absorption is said to have a STAR (naturally Surface Texture and enhanced Absorption with a back Reflector) structure.

At present, two types of light trapping

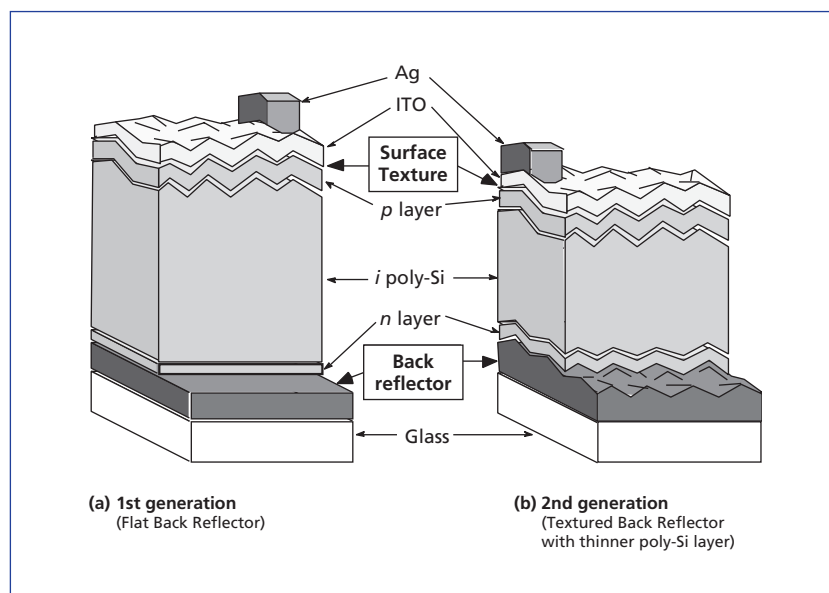


Fig. 5: Cross-sections through light-trapping microcrystalline silicon solar cell devices. (a) First generation (flat back reflector); (b) Second generation (textured back reflector, thinner polycrystalline silicon layer).

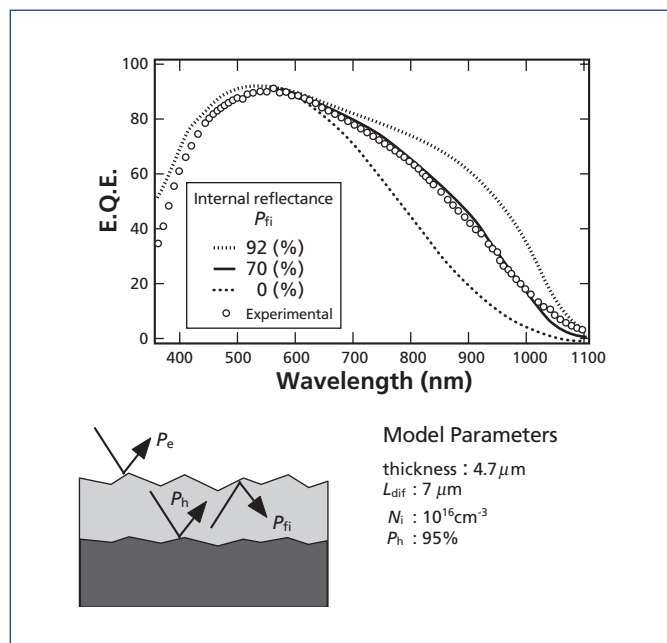


Fig. 6: Absorption efficiency of a 4.7 μm cell. In this figure, the open circles indicate measurement results. The solid, dotted and dashed lines show the spectra calculated using a PC1D.¹⁶⁾ The surface internal reflectivity P_{fi} (indicating the ratio of trapped light) was 0, 70 and 92% respectively. In the figure, P_e represents the surface reflectivity, and P_h represents the back surface reflectivity.

structure are in use. **Figure 5(a)** shows a cell that uses a flat highly reflective layer at the back surface, and **Fig. 5(b)** shows a cell that uses a textured type of highly reflective layer. This highly reflective back layer also acts as the solar cell's back electrode. Thin-film polycrystalline silicon forms naturally with a textured structure on its surface, and the size of

this texture is strongly dependent on the film thickness. When the film is relatively thick (4 μm or more), the surface texture is suitable for light trapping, but when the film is relatively thin (1.5 μm or less), an adequate surface texture does not form.⁸⁻¹¹⁾ It is this necessary to use a textured reflective layer at the back surface. Of course, to be precise the

texture characteristics depend on the fabrication conditions as well as the film thickness.

Cells of this sort are fabricated as follows. First, after a back reflector layer has been formed on a glass substrate, a layer of n-type silicon is deposited on it by plasma CVD. Next, the active layer, which is a thin film of intrinsic polycrystalline silicon, is formed by plasma CVD. Finally, a p-type silicon film and an ITO (indium tin oxide) film are deposited in turn, and then a comb grid electrode is formed on top.

Figure 6 shows the results of investigating the collection efficiency of cells with a 4.7 μm thick active layer. In this figure, the open circles indicate measured results. At longer wavelengths, this cell exhibits excellent sensitivity characteristics, and under an AM1.5 light source it was found to generate a current density in excess of 27 mA/cm^2 .^{10,11)} The solid, dotted and dashed lines in the figure show the spectra calculated using a PC1D.¹⁶⁾ These are the results obtained by changing the surface internal reflectivity P_{fi} to 0, 70 and 92% respectively, and are used as a parameter to express the light trapping ratio of the cell. A value of 95% is assumed for the back reflection rate. The other parameters are as shown in the Figure.

Changing the surface internal reflectivity causes the spectra to change in the wavelength region above 600 nm where the light is reflected from the back surface of the cell and surface effects are apparent. As the sur-

face internal reflectivity increases, the sensitivity to infrared light increases. From the experimental results and calculated results, the surface internal reflectivity of this cell corresponds to 70%.

Now consider the light trapping effect of a thin film polycrystalline silicon layer with a thickness of just 1.5 μm . **Figure 7(a)** shows the reflection spectra of samples corresponding to two types of 1.5 μm thick cell (one with a flat back reflector and one with a textured

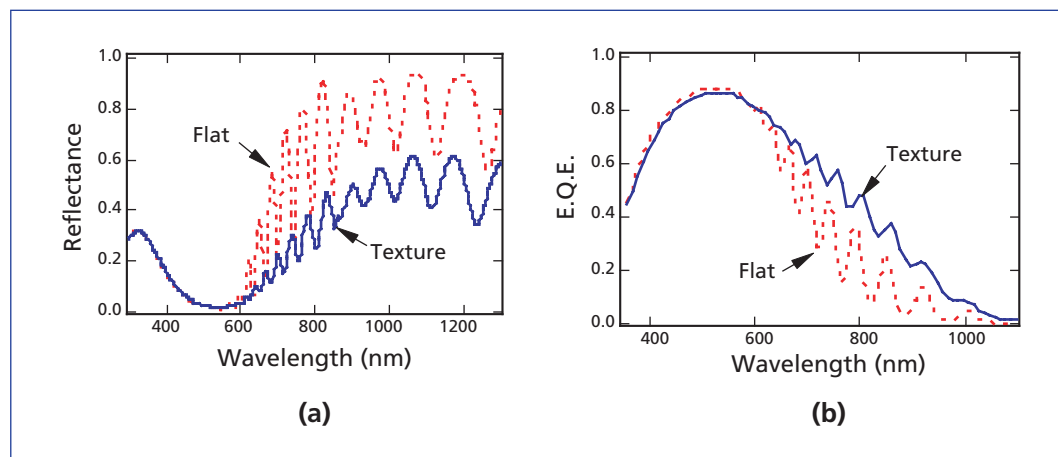
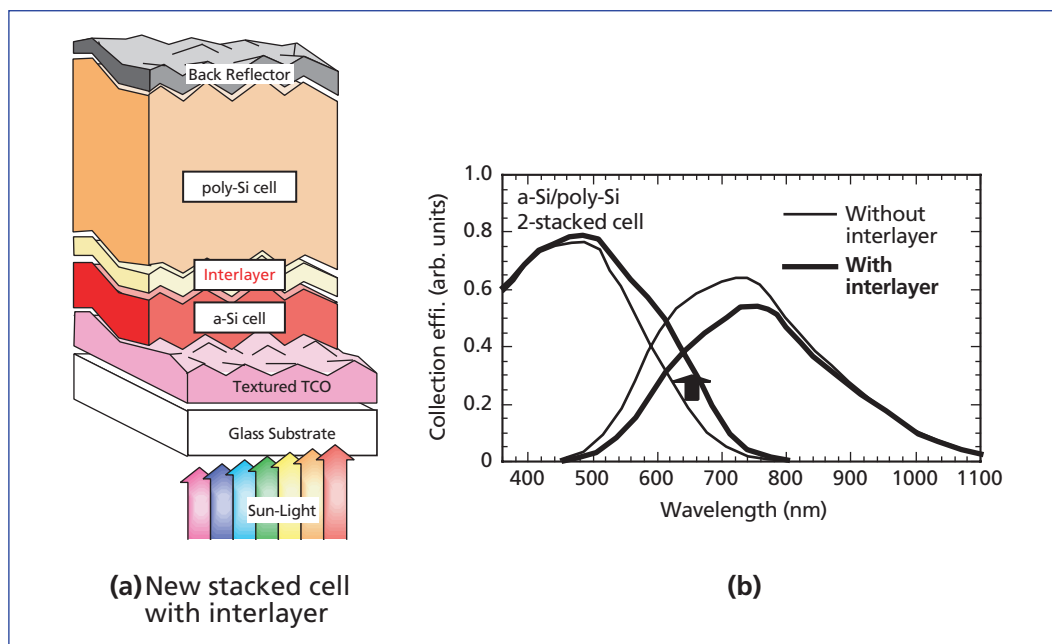


Fig. 7: The characteristics of microcrystalline solar cells on glass substrates having flat and textured back reflectors. (a) Reflectivity, and (b) collection efficiency characteristics (quantum efficiency).

Fig. 8: A next-generation tandem model. (a) Device cross-section of an amorphous – microcrystalline silicon layered next-generation tandem cell having a transparent intermediate layer (next-generation silicon hybrid cell); (b) Spectral sensitivity characteristics of the hybrid cell including the intermediate layer (absorption efficiency).



back reflector), and **Fig. 7(b)** shows the corresponding collection efficiency spectra.

In **Fig. 7(a)**, the minimum that appears in the spectra at around 550 nm arises because the ITO film was deposited under non-reflective conditions. The oscillation seen at wavelengths above 600 nm is caused by interference with the silicon film in the active layer. The reflectivity of the sample with the textured back surface is significantly lower in the infrared region. **Figure 7(b)** shows the spectral sensitivity spectra corresponding to the flat and textured samples. In the case of the textured sample, it can be seen that the sensitivity is higher at wavelengths above 600 nm, which corresponds to the reduction of the reflectivity spectrum at longer wavelengths.

This result provides experimental verification of the contribution made by minute textured structures to light trapping. In the future, it will be necessary to aim at increasing the efficiency by obtaining larger currents in the thin film through the formation of better light trapping structures by controlling the profile of the microcrystalline silicon surface and the underlying reflective layer.

3. Application to Stacked (Hybrid) Type Solar Cells

3.1 Silicon hybrid solar cells

Although the microcrystalline silicon cells formed at low temperature as de-

scribed above have a potential for high efficiently, their efficiency in single-cell structures is currently only about 10%, which is much lower than that of bulk polycrystalline cells. To achieve a substantial improvement of efficiency there needs to be some kind of breakthrough, such as a substantial reduction in the abovementioned grain boundary recombination or the establishment of more advanced light trapping techniques. In an attempt to achieve this, we have investigated the use of two- and three-stacked (hybrid) structures in which multiple cells with different light absorption characteristics are stacked together. This approach allows better characteristics to be obtained with existing materials and processes. The advantages of using a layered structure include the following: (1) it is possible to receive light by partitioning it over a wider spectral region, thereby using the light more effectively; (2) it is possible to obtain a higher open-circuit voltage; and (3) it is possible to suppress to some extent the rate of reduction in cell performances caused by optical degradation phenomena that are observed when using amorphous silicon based materials.

At the PV Research Division, we have recently made further progress with the investigation of stacked (tandem) cells in which the abovementioned amorphous silicon cells are combined with microcrystalline silicon cells, and have been studying structures in which a

transparent intermediate layer is provided between the amorphous silicon layer of the top cell and the microcrystalline silicon layer of the bottom cell (next-generation hybrid solar cell).

Figure 8(a) illustrates the structure of such a device. Compared with a conventional hybrid cell, the presence of a transparent intermediate layer, by its nature, causes some of the light that reaches the microcrystalline silicon layer of the bottom cell by passing through the amorphous silicon layer of the top cell to be reflected back into the top cell (amorphous silicon). As a result, the effective light sensitivity of the top cell is higher than that of a top cell with the same thickness in a conventional hybrid structure, so it is possible to expect an improvement in the short-circuit current J_{sc} of the overall hybrid cell. **Figure 8(b)** shows how the sensitivity spectrum of the hybrid cell is affected in practice by the addition of a transparent intermediate layer. Even if the amorphous silicon and microcrystalline silicon layers have the same thickness, the cell with a transparent intermediate layer is more sensitive at shorter wavelengths (top cell).

This result seems to suggest the possibility of controlling the respective light sensitivities of the top and bottom cells by introducing a suitable transparent intermediate layer. From the results of **Fig. 8(b)** it can be inferred that by controlling the thickness of the

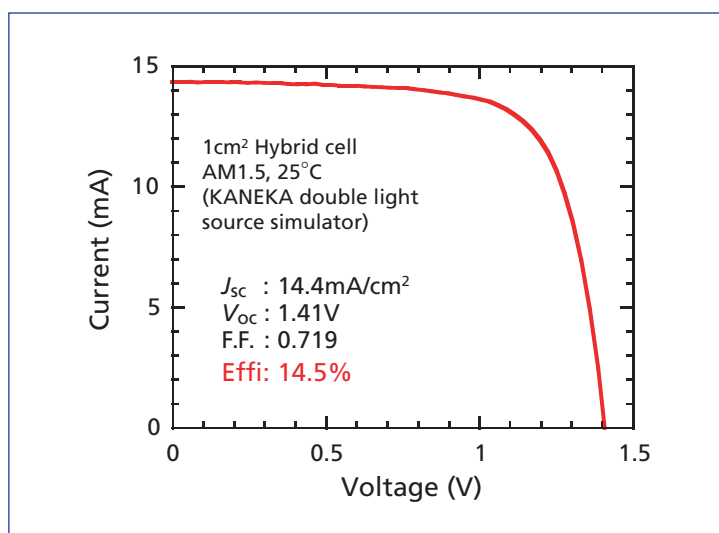


Fig. 9: Current-voltage characteristic of an amorphous – microcrystalline silicon stacked next-generation hybrid cell with a transparent intermediate layer (initial efficiency; area 1 cm²).

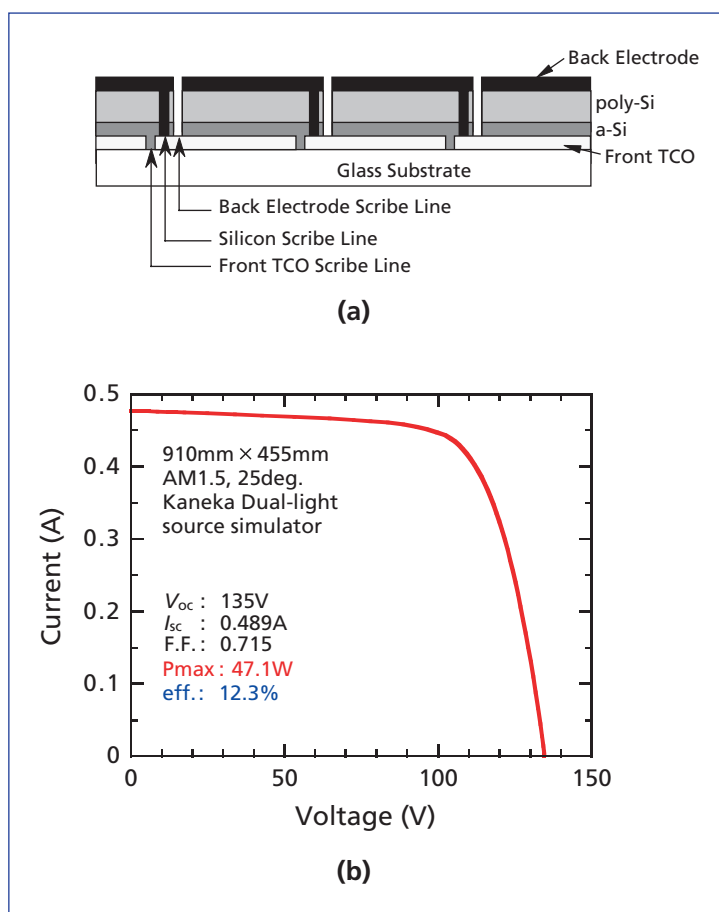


Fig. 10: A silicon hybrid cell. (a) Cross-sectional structure of the silicon hybrid module (amorphous – microcrystalline silicon tandem solar cell module; series-connected). (b) Current-voltage characteristics of a large area (910x455 mm) silicon hybrid module (initial efficiency).

transparent intermediate layer it is possible to reduce the thickness of the top cell needed to obtain the same current compared with a conventional hybrid cell. As a result, it should be possible to obtain roughly the same short circuit current J_{sc} even when the amorphous silicon film thickness is reduced. If the thickness of the amorphous silicon film in the top cell can be reduced, then it should also be possible to reduce the photo-degradation of cell.

This structure (amorphous silicon – transparent intermediate layer – microcrystalline silicon) thus makes it possible to improve not only J_{sc} but also the cell characteristics compared with a conventional hybrid cell with no transparent intermediate layer without reducing V_{oc} or the fill factor (FF). As Fig. 9 shows, an initial conversion efficiency of 14.5% has been achieved with a 1 cm square small area cell of this type.¹⁸⁾

3.2 Large area thin film silicon hybrid modules

At the PV Research Division, we have begun developing techniques for depositing microcrystalline silicon films on large area substrates, and for the production of silicon hybrid modules based on tandem cells of amorphous silicon and microcrystalline silicon.^{19,20)} We have also been developing mass production techniques, which were put into commercial operation in 2001. These hybrid modules employ a super-straight structure in which light is incident through a glass substrate on which a transparent electrode is formed, and are integrated by laser scribe processing (Fig. 10(a)). By adding a microcrystalline silicon film deposition process, the amorphous silicon module production process can be used to fabricate silicon hybrid modules.

As a result of improving the efficiency of a large area hybrid module measuring 910 × 455 mm, we have achieved an initial efficiency of 12.0% and a peak output power of 46.0 W as shown in Fig. 10(b). We have also achieved the goal of a film deposition rate of 1.1 nm/s on metro-size large area substrates. The efficiency of these cells is somewhat lower (11.2%), but still of practical use.²¹⁾ Some of these modules are shown in Fig. 11.

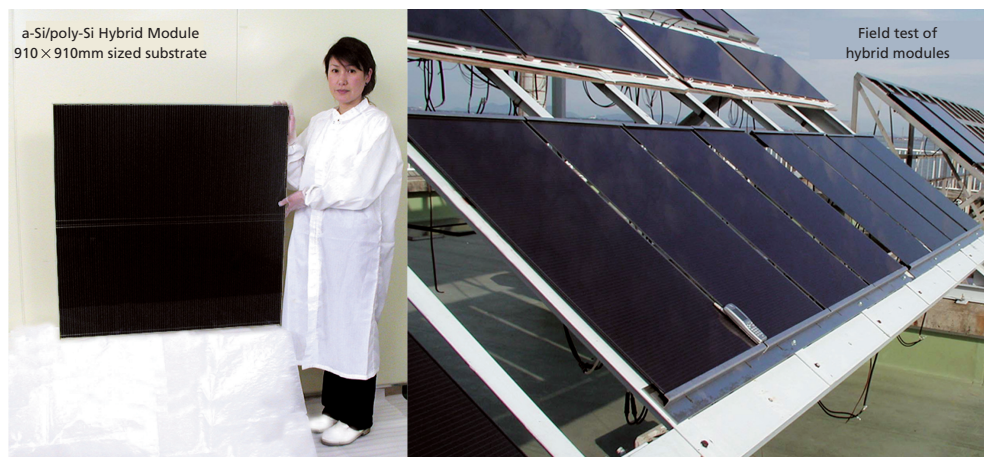


Fig. 11: Appearance of the hybrid modules.

4. Conclusion

It has been demonstrated that microcrystalline silicon with a very small grain size formed at low temperature by plasma CVD is a promising material for use in solar cells. Amorphous solar cells and stacked silicon (hybrid) solar cells have already been put to practical use in power modules. Further study is needed to ascertain and control the relationship between recombination at grain boundaries and the grain boundary microstructure, which is a non-uniform system. This should make it possible to improve the inherent performance of microcrystalline silicon solar cells. There is also a need for the development of crystal deposition methods that allow some degree of control over the texture structure of the silicon surface to allow a suitable level of light trapping to be implemented.

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[JSAP](#)

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Joined Kaneka Corporation in 1983 on completing a master's course in engineering at Kyoto University. From 1988 to 1990 he was a guest researcher at Stamford University, and in 1991 he was awarded a D. Eng. Since 1991 he has been engaged in the study of silicon thin-film solar cells. A member of the American Physical Society (APS) and the Institute of Electrical and Electronics Engineers (IEEE).

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