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(56) Related Art
X. Deng et al., 'VHF Plasma deposition of microcrystalline-Si p-layer materials'
B. Rech et al., 'New materials and deposition techniques for highly efficient silicon thin film solar cells'
Rudd E. I. Schropp et al., 'Novel profiled thin-film polycrystalline silicon solar cells on stainless steel substrates'
Luc Feitknecht et al., 'Plasma deposition of thin film silicon: Kinetics monitored by optical emission spectroscopy'
Tobias Repmann et al., 'Development of A-Si:H / microcrystalline-Si:H thin film solar modules using 13.56 MHz PECVD'
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Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: METHOD FOR DEPOSITING SILICON

(54) Bezeichnung: VERFAHREN ZUR ABSCHIEDUNG VON SILIZIUM

(57) Abstract: The inventive method for depositing silicon onto a substrate firstly involves the introduction of a reactive silicon-containing gas and hydrogen into the plasma chamber and then the initiation of the plasma. After initiating the plasma, only reactive silicon-containing gas or a gas mixture containing hydrogen is supplied to the plasma chamber in an alternatively continuous manner, and the gas mixture located inside the chamber is, at least in part, simultaneously withdrawn from the chamber. From the start, homogeneous microcrystalline silicon is deposited onto the substrate in the presence of hydrogen.

(57) Zusammenfassung: Das erfindungsgemäße Verfahren zur Abscheidung von Silizium auf einem Substrat legt in der Plasmakammer zunächst ein reaktives siliziumhaltiges Gas und Wasserstoff vorstartet und dann das Plasma. Nach dem Plasmastart wird der Plasmakammer alternativ kontinuierlich nur reaktives siliziumhaltiges Gas oder eine Gas Mischung mit Wasserstoff zugeführt, und gleichzeitig das in der Kammer vorliegende Gasgemisch zumindest teilweise aus der Kammer abgeleitet. In Anwesenheit von Wasserstoff scheidet sich dabei homogen mikrokristallines Silizium auf dem Substrat von Anfang an ab.

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METHOD OF DEPOSITING SILICON

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The invention relates to a method for depositing microcrystalline silicon coatings and especially to a method of depositing microcrystalline silicon in which only a small amount of hydrogen is required.

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State of the Art

Microcrystalline silicon is a material which is used especially in solar cells as an absorber material. It is produced today in many laboratories by means of the PECVD (plasma enhanced chemical vapor deposition) from a silane and hydrogen. The supply of hydrogen, the so-called hydrogen dilution, is here
15 necessary to produce crystalline silicon at substrate temperatures below 500EC. These crystalline silicon coatings are comprised of many microscopically small crystallites and thus the name "microcrystalline silicon."

Microcrystalline silicon can be deposited in various deposition regimens as high value coatings. In the deposition with PECVD using the standard industrial
20 frequency 13.56 MHz the silane

concentration (= silane flow/hydrogen flow) is typically about 1% and at excitation frequencies in the VHF range is as a rule less than 10%. The hydrogen is required in order to influence growth of the coating. However, only a small part of the hydrogen used is incorporated in the silicon layer to be produced, typically less than 10%. The remaining hydrogen is pumped off. For a later industrial production, the high hydrogen consumption, especially for deposition at 13.56 MHz is a significant problem because of its high cost^[1].

From the state of the art, the following important methods of depositing microcrystalline silicon by PECVD with reduced hydrogen consumption are known.

1. The "Closed-chamber CVD process" (CC-CVD)^[2]:

This investigated process runs cyclically (discontinuously) and encompasses basically two process steps. In a first step a small amount of the reactive process gas (SiH_4 or CH_4/SiH_4 mixture) flows in a ratio of about 25% reactive gas to hydrogen through the chamber. This step serves to refresh the gas atmosphere after a process cycle. During this time the plasma burns with reduced power (about 10 W) so that an ultrathin silicon layer is deposited.

In the subsequent second step, both the pump power from the chamber and also the gas supply into the chamber are interrupted. By delaying the shutoff of the hydrogen feed, the deposition pressure is increased and the silane concentration lowered to about 5%. The plasma burns for about 60 watts more. The

process gas is gradually decomposed and the deposited layer grows further.

At the same time a contrary effect arises. The coating is etched by hydrogen radicals. The etch rate increases continuously because of the increasing proportion of hydrogen in the plasma until finally an equilibrium between the coating growth rate and the etching is reached. Atoms which are the most weakly bound are preferably etched so that finally a network of strongly bound material is formed.

The entire deposition process is carried out as a continuous repetition of these two steps in succession (layer by layer) until the desired coating thickness is achieved. The volume proportion of crystallites is greater than 90%. Because of the cyclical variation in the process conditions, this process is however very expensive. It differs basically from the standard PECVD process used and has until now not been found to be suitable in industry. With this process up to now, it also has not been possible to make solar cells.

2. The "Static closed chamber Process" (VHFGD)^[3]:

This very high frequency glow discharge (VHFGD) deposition process is a continuous process without continuous input of hydrogen. The deposition chamber (plasma chamber) is not completely isolated. A small flow of silane is admitted into the chamber and a corresponding amount of gas is simultaneously pumped off. The deposition is effected with VHF excitation and at reduced pressure (0.1 mbar). In the deposition of silicon from the silane,

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hydrogen is liberated. The reduced silane gas flow ensures that a silane-poor state develops. The initial rapid deposition of silicon is braked by the increase in dissociated hydrogen. After about one minute, static conditions prevail with a small ratio of $[\text{SiH}^*]/[\text{H}_a]$ at which a continuous microcrystalline growth is possible.

Since the deposition is started with a pure silane plasma and only later does hydrogen arrive from the decomposition of the silane, the deposited layer has a significant amorphous incubation layer (about 10 nm) as a first layer. This can result in a significant detriment to the function in the use of such coatings in electronic components, especially in solar cells. Thus solar cells whose i-layer is made by this process only have an efficiency of 2.5%.

The invention seeks to provide a method of making microcrystalline silicon coatings which on the one hand have a substantially homogeneous microcrystalline structure in the direction of coating growth, that is structurally homogeneous characteristics and on the other hand use only small amounts of hydrogen.

Accordingly, the present invention provides a process for depositing microcrystalline silicon on a substrate in a plasma chamber, which process comprises:

- (a) providing a reactive silicon containing gas and hydrogen in the plasma chamber before starting a plasma;
- (b) starting a plasma;
- (c) continuously and exclusively feeding reactive silicon containing gas to the chamber after the plasma starts or continuously feeding a mixture of a reactive silicon-containing gas and hydrogen to the chamber after the plasma start with the concentration of reactive silicon containing gas in the chamber is greater than 3%;
- (d) removing from the chamber an amount of gas corresponding to the gas mixture fed into the chamber;
- (e) whereby the total flow of gases (sccm) introduced into the plasma chamber, with respect to the surface to be coated of the substrate (100 cm^2) in relation to the deposition rate (nm/s) does not exceed a value of $1 [\text{sccm} \cdot \text{s}/\text{cm}^2]$.

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nm]; and

(f) selecting an excitation frequency for the plasma of less than 50 MHz and deposition pressure of greater than 3 mbar.

The formation of homogeneous microcrystalline silicon coatings, especially as a first layer on a substrate, can be effected in a plasma deposition chamber only in the presence of corresponding amounts of hydrogen.

This means that already at the beginning of a deposition, hydrogen must be provided for a crystalline growth to be effected advantageously from the start. In the framework of the invention, a process has been developed whereby overall there will be a small hydrogen consumption. But nevertheless sufficient oxygen will be made available from the beginning of the deposition. In a continuous process, advantageously only small amounts of hydrogen are introduced. Advantageously, during the deposition process steady static (steady-state) deposition conditions are established. This is accomplished, among other things by a controlled feed and discharge of the corresponding gases into and from the plasma chamber. At the beginning of the deposition process, the ratio of the reactive silicon containing gas to hydrogen of less than 0.5 and especially of less than 0.25 has been found to be generally effective. As the reactive silicon containing gas for this process, especially silanes can be mentioned. Higher silanes, for example disilane, (Si_2H_6) chlorosilane and fluorosilanes, for example SiCl_4 or SiF_4 , as well as their higher forms and mixed forms, for example, dichlorosilane (SiCl_2H_2) are also conceivable. The excitation frequency for the plasma should advantageously be smaller than 50 MHz, especially smaller than 30 MHz. When the

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deposition is carried out with PECVD, for example, a standard industrial frequency of 13.56 MHz is used.

A first embodiment of the invention provides initially a mixture of hydrogen and a reactive silicon-containing gas, especially silane, at the starting conditions within the deposition chamber. This can be achieved for example either by a) the continuous traversal of the plasma chamber by a corresponding gas mixture of silane and hydrogen, or however also b) by a one-time flooding of the previously evacuated plasma chamber with a gas mixture.

Simultaneously with the starting up of the plasma, in case a) the hydrogen feed is terminated.

In a further part of the process, after the plasma start up has occurred, the silane in the chamber is disassociated by the plasma and consumed in the deposition process and thus is replaced by the continuous feed of the silane to the chamber. To maintain static [steady-state] pressure conditions (deposition pressure) within the plasma chamber. A corresponding amount to the gas mixture fed must be removed from the chamber. In the presence of hydrogen there is a microcrystalline growth of the silicon coating on the substrate from the start.

Since the absolute gas flux which is adjusted will depend on the respective size of the plasma chamber the gas flow in accordance with the invention is set depending upon the substrate area to be coated. The gas flow after the start up of the plasma of the reactive silicon containing gas lies advantageously in the

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been found to be highly suitable for use as absorber layers in a solar cells, for example solar cells having an efficiency of more than 5%.

It has been found to be especially advantageous because the process can be carried out in the narrow process window which is required for solar cells with
5 high efficiency for suitable coatings.

The invention also provides a substrate comprising microcrystalline silicon deposited thereon when produced by the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

10 In the following the subject matter of the invention will be described with reference to three figures as well as two embodiments in greater detail, without limiting the scope of the invention thereto. The figures are:

FIG. 1 the solar cell characteristic values

- a) efficiency η ,
- b) filling factor FF,
- c) no load (open circuit voltage V_{oc}) and
- d) short circuit current density J_{sc} , all as a function of the silicone concentration $[SiH_4]/[H_2]$.

The solar cells were produced at a deposition pressure $p_{dep} = 11$ mbar and a plasma energy of $P_{HF} = 0.26$ W/cm² and had an absorber layer thickness of about 1.1 μ m (according to Repmann^[4]).

FIG. 2: Silane flow (squares) and silane concentration (open triangles) for the fuel cells with optimized fabrication (corresponding to FIG. 1) at different hydrogen fluxes. The solar cells were coated at 27 mbar and 0.7 W/cm² with the absorber layers.

FIG. 3 the quantum efficiency of a solar cell with 7.3 % efficiency with an i-layer produced without feed of hydrogen (Example A).

FIG. 1 describes the relationship of the solar cell parameters with variation of the silane concentration during the i-layer growth (absorber at a certain silane concentration here about 0.9%) a maximum efficiency is obtained. This silane concentration is not only of significance for solar cells but is also the high silane concentration at which under the given conditions microcrystalline silicon can be produced with a high volume proportion.

In FIG. 2 the maximum silane flow for a given hydrogen flow in a continuous process for microcrystalline growth and the

resulting silane concentrations have been given. The optimization is effected in accordance with FIG. 1. With these concentrations of silane flow and hydrogen flow at the indicated pressures and powers the respective homogeneous growths of microcrystalline silicon coatings (at high volume proportion of crystals) is possible.

FIG. 3 shows the quantum efficiency of a solar cell in which during the deposition hydrogen was no longer supplied the higher quantum efficiencies are indicated in the long wave (>800 nm) portion of the spectral range) showing that the i-layer has a high crystalline volume proportion.

In the following, two embodiments of the process of the invention are described in greater detail.

Both embodiments relate to a respective substrate area of 100 cm².

A) In a first embodiment of the process a mixture of hydrogen and silane (in accordance with standard conditions, that is a silane-hydrogen mixture according to FIG. 2 is introduced in order to ensure defined starting conditions before the commencement of the deposition.

Since at the start hydrogen is provided, the microcrystalline growth begins at the outset. After the start of the plasma the hydrogen flow is shut off. The consumed silane is replaced by a slight influx of silane. Hydrogen is present for the entire time since on the one hand the hydrogen present at the beginning in the chamber is only consumed to a small degree and is

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only partly pumped off and on the other hand during the deposition of silicon from the silane new hydrogen is continuously released ($\text{SiH}_4 \rightarrow \text{Si}(\text{coating}) + 2\text{H}_2$). The exhaust pumping is so controlled over the entire period that the deposition pressure remains constant. An optimization of the process is effected through the choice of suitable starting conditions and through the choice of the silane flow during the deposition.

The process is thus comprised of two steps:

1. The establishment of the deposition pressure with high hydrogen flow and reduced silane flow (without plasma).

2. The deposition under an influx exclusively of silane.

In the selected embodiment or example, at $p = 27$ mbar, a gas mixture with the ratio $[\text{SiH}_4]/[\text{H}_2]$ of 2.4 sccm/360 sccm was admitted into the chamber. With the starting of the plasma (13.56 MHz plasma) the supply of hydrogen was stopped. The silane flow established after the start of the plasma was 1 sccm.

The silicon was deposited upon the substrate at a power of 0.7 W/cm^2 . The thickness of the coating deposited amounted to $1.8 \mu\text{m}$ with a deposition rate of 1.7 \AA/s .

The microcrystalline layer made by this process was completely incorporated in a solar cell. The thus fabricated solar cell had an efficiency of 7.3% (FF = 62.6 %, $V_{oc} = 490 \text{ mV}$, $J_{sc} = 23.9 \text{ mA/cm}^2$). In FIG. 3 the quantum efficiency of the fabricated solar cell has been given. The high short circuit and the high quantum efficiency for wavelengths greater than 800 nm are an indication of the high volume proportion of crystallinity over the entire i-coating thickness. If the ratio of the consumed silane to the hydrogen used to build hold up the pressure is of interest for this cell, one obtains a ratio of 4:3.

B) In a further embodiment of the process a mixture of silane and hydrogen as process gas was continuously used. At extremely low total gas flow the porosity of silane which results, leads to a microcrystalline growth also at low hydrogen flow rates.

In the selected embodiment the solar cell was produced with deposition conditions 1 sccm SiH_4 , 4 sccm H_2 , 27 mbar, 0.7 W/cm^2 . The solar cell had an efficiency of 7.0% (FF = 69.1%, $V_{oc} = 485 \text{ mV}$, 21.0 mA/cm^2 at a deposition rate

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of 2.4 Å/s.

The cited literature in this application:

- [1] A. V. Shah et al., Solar Energy Materials and Solar Cells, in print (2003).
- 5 [2] S. Koynov et al., Thin Solid Films 383 (2001) 206 - 208. S. Koynov et al., Jpn. J. Appl. Phys. 33 (1994) 4534 - 4539.
- [3] L. Feitknecht et al., Solar Energy Materials and Solar Cells, 74 (2002) 539 - 545.
- [4] T. Repmann et al., Proc. Of the 28th IEEE Photovoltaic Specialists
- 10 Conf., S. 912 - 915 (2000).

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any

15 other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the

20 common general knowledge in the field of endeavour to which this specification relates.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for depositing microcrystalline silicon on a substrate in a plasma chamber, which process comprises:
 - 5 (a) providing a reactive silicon containing gas and hydrogen in the plasma chamber before starting a plasma;
 - (b) starting a plasma;
 - (c) continuously and exclusively feeding reactive silicon containing gas to the chamber after the plasma starts, or continuously feeding a mixture of a
 - 10 reactive silicon-containing gas and hydrogen to the chamber after the plasma start with the concentration of reactive silicon containing gas in the chamber is greater than 3%;
 - (d) removing from the chamber an amount of gas corresponding to the gas mixture fed into the chamber;
 - 15 (e) whereby the total flow of gases (sccm) introduced into the plasma chamber, with respect to the surface to be coated of the substrate (100 cm^2) in relation to the deposition rate (nm/s) does not exceed a value of $1 [\text{sccm} \cdot \text{s}/\text{cm}^2 \cdot \text{nm}]$; and
 - (f) selecting an excitation frequency for the plasma of less than 50
 - 20 MHz and deposition pressure of greater than 3 mbar.
2. The process according to claim 1, wherein the total flow of gases introduced into the plasma chamber does not exceed a value of $0.6 [\text{sccm} \cdot \text{s}/\text{cm}^2 \cdot \text{nm}]$.
- 25 3. The process according to claim 1 or 2, wherein the flow of gas or gas mixtures to the chamber and gas or gas mixture discharged from the chamber are controlled so that during the process a constant deposition pressure is achieved.
- 30 4. The process according to any one of claims 1 to 3, wherein before start of the plasma the ratio of reactive silicon containing gas to hydrogen is less than 0.5.

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5. The process according to claim 4, wherein the ratio is less than 0.25.
6. The process according to any one of claims 1 to 5, wherein silane is used as the reactive silicon containing gas.
- 5 7. The process according to any one of claims 1 to 6, wherein an excitation frequency for the plasma of less than 30 MHz is selected.
8. The process according to any one of claims 1 to 7, wherein a deposition
10 pressure of greater than 6 mbar is selected.
9. The process according to any one of claims 1 to 8, wherein exclusively reactive silicon-containing gas is continuously fed to the chamber after the plasma start at a volume flow of 0.5 sccm up to 20 sccm/100 cm² of surface to be coated.
- 15 10. The process according to claim 9, wherein the volume flow is 0.5 sccm to 5 sccm/100 cm² of coating surface area.
11. The process according to any one of claims 1 to 10, wherein absorber
20 layers for solar cells with an efficiency of more than 5% are produced.
12. The process of claim 1 substantially as hereinbefore described.
13. A substrate comprising microcrystalline silicon deposited thereon when
25 produced by the process claimed in any one of claims 1 to 12.

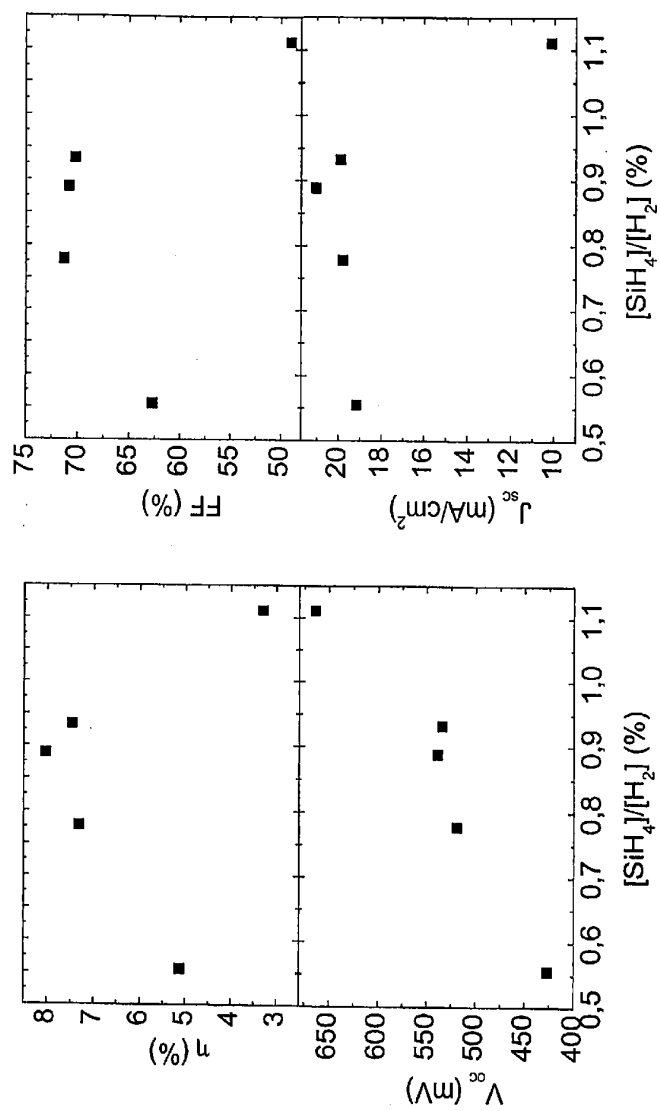


Fig. 1

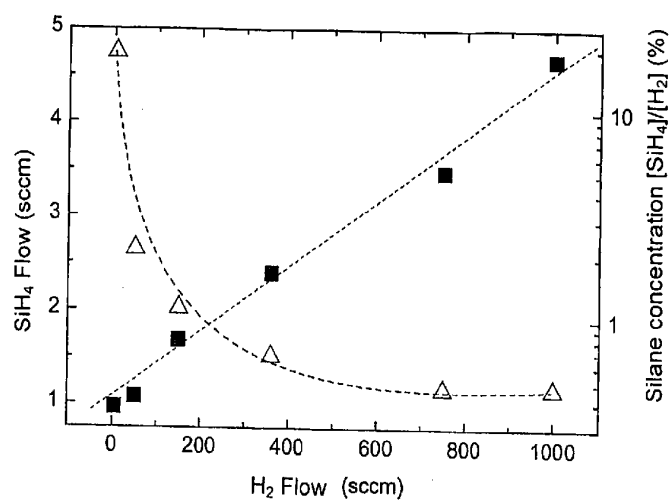


Fig. 2

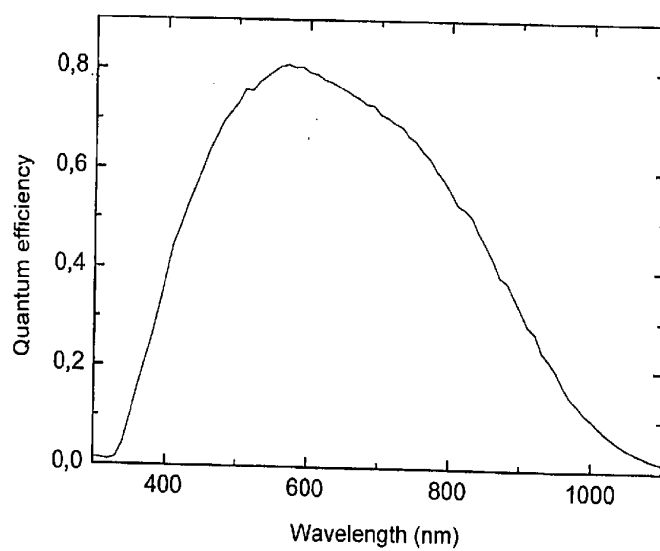


Fig. 3