OPTO-ELECTRONICS REVIEW 9(1), 91–95 (2001)

UHV plasma enhanced CVD system for preparation of new generation amorphous silicon based efficient solar cells

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Plasma enhanced chemical vapour deposition (PECVD) is used in the deposition of various thin films such as amorphous silicon, nitrides, oxides and diamond-like carbon. The authors succeeded in preparation of photovoltaic intrinsic a-Si:H with density of states of 10^{16} cm^{-3} and high photoconductivity gain. These films are the constituents of homojunction p-i-n solar cells or heterojunction type with silicon-carbon window layer of efficiency over 10%. The microwave plasma chemical vapour deposition (MWCVD) seems to be a promising method for the deposition of passivation layers.

Key words: amorphous silicon, plasma enhanced chemical vapour deposition, microwave plasma chemical vapour deposition, passivation, solar cells.

1. Introduction

Thin films for solar cells application should be characterised by uniformity of chemical content, high chemical stability, and proper electrical and optical properties. These properties are obtained by the use of certain specific technologies in the deposition processes. Thin films for solar cells are mainly deposited by CVD and PVD methods in various system configurations [1,2]. The well known technique of plasma enhanced radio frequency CVD is one of the promising and effective methods for deposition of the semiconducting active layers in photovoltaic devices for large scale solar cells production. The deposition of other layers in solar cells structures and other optoelectronic devices does not need ultra high vacuum that facilitates the technological process [3]. Although the technique of Microwave plasma CVD (MWCVD) is still a developing method the authors believe that it could be effectively applied for deposition of antireflective and buffer layers.

2. Deposition system

The thin film microwave chemical vapour deposition (MWCVD) and plasma enhanced chemical vapour deposition system is located at the University of Mining and Metallurgy, Faculty of Materials Science and Ceramics. It was funded by the State Committee for Scientific Research in Warsaw in the frame of the project and was designed by Dr P. Rava and constructed at Elettrorava S.p.A. in Italy. The system consists of two process chambers with manual substrate loading, retrofittable with a load lock chamber to allow substrate loading and unloading in the process chambers without breaking vacuum. The system uses separate gas inlet manifolds and vacuum pumping systems for each of the process chambers, to ensure the best possible separation and avoidance of cross-contamination between the chambers. The high vacuum pumping as well as the process gas pumping in the PECVD chamber is provided via a turbomolecular pump to prevent the possibility of back streaming of rotary pump oil. The process chambers are constructed in accordance with UHV system practices.

The major features of the system are as follows:

- in the MWCVD chamber ultimate pressure 10^{-4} Torr, substrate size 10×10 cm^2, downward deposition of thin films, microwave 2 kW plasma source. In the PECVD chamber an ultimate pressure 10^{-9} Torr can be obtained and plasma is activated in upward deposition mode by an RF 13.56 MHz 300 W generator. The substrate of 10×10 cm^2 size can be heated up to 350°C. The system of gas dosing consists of a manifold with 7 separate gas (vapour) lines and is designed for retrofit of additional gas lines. The system is provided with a number of interlock circuits to prevent the release of toxic gases.
- the MWCVD chamber is provided with numerous accessories: thermocouple, capacitance manometers, manipulator for substrate height adjustment, rails for substrate carrier, gas inlet and distribution system and an N_2 backfill port. The stainless steel process chamber has dimensions: 350 mm diameter, 700 mm height, and is water-cooled. In the MWCVD chamber a vacuum compatible heater using a pyrolytic graphite heater with boron nitride insulators (Advanced Ceramics, approx. size 110×110 mm^2) is placed just below the substrate

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frame, to provide substrate temperature heating up to 1500°C. A type C thermocouple is embedded into the top boron nitride insulator. A PID temperature controller Eurotherm 2208 is provided.

- PECVD stainless steel chamber of diameter 250 mm and height 335 mm is provided with bottom removable flange, gas inlet and distribution system, capacitance manometer, throttle valve, top removable flange with heater, K-type thermocouple with Eurotherm regulator, rails for substrate carrier, and RF electrode. The height of the electrode is adjustable; the recommended electrode to substrate distance is in the range 10–50 mm. A flange on the side wall for the load port and future retrofit with gate valve and load lock and two viewports are provided.

Vacuum pumping and pressure control

The MWCVD chamber is pumped by a Roots blower pump and a rotary pump, the PECVD chamber is pumped by a turbomolecular pump. The pumping system of the MWCVD chamber consists of a double stage rotary pump Edwards E2M40 with chemical filter, a booster roots blower Edwards EH250, pumping speed 250 m^3/h, a throttle valve for automatic pressure control MKS 653, two capacitance manometers.

The PECVD chamber is equipped with a turbomolecular pump Elettrorava ETP 300CR (corrosion resistant of pumping speed 300 l/s) provided with automatic safety valve, a throttle valve, capacitance manometers MKS (for various pressure ranges), an ionisation gauge and a convectron gauge with associated controls (Granville Phillips).

The pumping units of both chambers are provided with a nitrogen purge system.

The gas manifolds

The system is supplied with a manifold for six following gases: Ar, N_2, CH_4, SiH_4, NH_3, H_2, one line of controlled vapour flow, a set of electropneumatic gas shut off valves for each gas line and relative electropneumatic actuators and a set of manual safety gas line evacuation valves. The gas manifold is modular and uses VCR sealed standard components. Manifold bypass lines are provided for emergency operations on the reactive gas lines. An inert purge gas is used to purge the process chambers before and after each deposition run. Two safety gas cabinets with VCR gas panels, station pressure regulators and pneumatically activated safety diaphragm valves improve the safety of the operation.

Microwave and RF sources

The MW source (Dual Plasmaline) consists of two antennas, inside two ceramic tubes at the distance of 580 mm, which are used to achieve uniform plasma over 10×10 cm^2. The MW generator 2 kW 2450 MHz is connected with the magnetron head which is water-cooled. A three-stub manual tuner enables proper distribution of microwave radiation. A RF generator 300 W 13.56 MHz with a matching network provides uniform plasma in the PECVD chamber, which guarantees uniformity of thin films on 10×10 cm^2 substrates.

3. PECVD thin films deposition

The PECVD system was designed for deposition of amorphous and microcrystalline silicon based alloys as well as of other materials such as amorphous carbon, DLC, silicon and carbon nitrides of promising optoelectronic and mechanical properties [4,5]. By the PECVD method the following photosensitive materials were deposited: amorphous silicon (a-Si:H), a-$Si_{1-x}C_x$:H, a-$Si_{1-x}N_x$:H, microcrystalline µc-Si:H and µc-$Si_{1-x}C_x$:H.

Although amorphous silicon technology has developed up to the point of mass production of solar cells, the improvement in the properties of the single thin films that are the solar cell constituents is still a current task. One of the outstanding problems is the possibility of obtaining device quality materials with different band-gaps for solar cell tandem structures. These structures lead to a better use of the solar spectrum. One candidate is a-$SiGe_x$ of lower band gap than a-Si:H but of poorer optoelectronic properties. This material can be replaced by microcrystalline silicon, as proposed and confirmed by the Neuchatel group [6]. The use of, so-called, hydrogen dilution in the PECVD process during the preparation of intrinsic active layers is one of the keys to improved properties. H_2 dilution influences the microstructure of thin films causing medium range order or microcrystallisation [7]. Amorphous $Si_{1-x}C_x$:H layers in tandem structure lower the reflection losses at CTO interface and reduce the absorption at short wavelengths. An a-$Si_{1-x}C_x$:H, $x = 0.1$ film was used as a constituent layer in solar cell prototype ($V_{oc} = 0.91$, $J_{sc} = 9.45$ mA/cm^2, FF = 0.55, $\eta = 4.7$) [8].

Based upon the previous experience of the one of the authors (P.R.) who installed and designed several PECVD systems (LAMEL-CNR Bologna, Utrecht University, Philips Redhill, ENEA) and took part in many projects for the deposition of homojunction p-i-n and tandem and heterojunction silicon based solar cells, the technological deposition conditions given below seem to be those typical for efficient solar cells prototypes. One of the conditions for the achievement of efficient solar cells is that the system should be equipped with dedicated UHV chambers with their own gas manifolds for PECVD deposition of intrinsic and doped materials. For p-type window layer (a-$Si_{1-x}C_x$:H): P = 4 W, temp. 130°C, SiH_4 32 sccm, CH_4 50 sccm, B_2H_6 (2% in H_2) 8 sccm, tot. pressure 0.8 Torr. For i- layers a-$Si_{1-x}C_x$:H ($x = 0.1$): P = 4 W, temp. 215°C, SiH_4 flow 40 sccm, CH_4 flow 50 sccm, tot. pressure = 0.8 Torr. For n-type a-Si:H: P = 4 W, temp. 215°C, SiH_4 60 sccm, PH_3 (2% in H_2) 20 sccm, tot. pressure 0.8 Torr.

The achievement of improved window layer of n-type microcrystalline µc-$Si_{1-x}C_x$:H needs the use of a hydrogen diluted gas mixture. The recommended conditions are as

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follows: SiH_4 flow 5 sccm, CH_4 0.5–1.5 sccm, H_2 – 200 sccm, PH_3 – 2200–8900 vppm, substrate temp. 200°C and total pressure 0.3 Torr. The deposition system described in previous section is suitable for the deposition of such films. Device quality a-Si:H films were deposited under the following conditions: SiH_4 flow – 40 sccm, T_s = 240°C, total pressure 0.6 Torr, RF power = 5 W, time 1 hour.

4. Properties of a-Si:H

The most important material properties from the photovoltaic point of view are disorder, defect density and normalised photoconductivity. The Urbach energy is a parameter depending strongly on the disorder and is defined as a displacement of atoms from the positions typical for ordered structure. The Urbach characteristic energy E_u is defined as

$$\alpha(E) = \alpha_0 \exp\left(\frac{E-E'}{E_u}\right), \tag{1}$$

where α_o and E' are the constants. The absorption curves $\alpha(E)$ were detected by both PDS (photothermal deflection spectroscopy) and optical transmittance and reflectance measurements. In Fig. 1 the absorption coefficient vs. photon energy for a-Si:H sample is presented. The calculated Urbach energy for all investigated films was in the range 57–65 meV, what confirms that these layers are good candidates for solar cell applications.

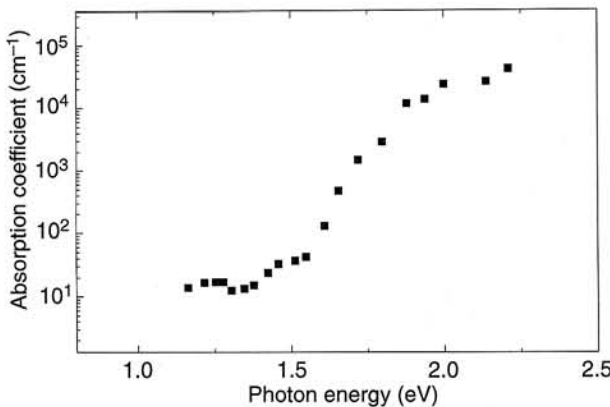

Fig. 1. Absorption coefficient vs. photon energy for device quality a-Si:H film deposited under the following conditions: SiH_4 flow – 40 sccm, T_s = 240°C, total pressure 0.6 Torr, RF power = 5 W, and time 1 hour.

The authors investigated the density of states in deposited intrinsic a-Si:H layers using both integrated absorption and modulated photocurrent method (MPC). In a-Si:H the unsaturated bonds are the main source of defects and are responsible for an excess in the absorption coefficient in the low energy region below the Urbach tail. The subgap absorption is a source of information on the number of defects: this can be estimated by separating the subgap absorption from the exponential band-tail absorption [9]. The excess optical absorption α_{ex} is given by

$$\alpha_{ex} = \alpha - \alpha_0 \exp\left(\frac{h\nu}{E_u}\right), \tag{2}$$

where α_o and E_u are the constants graphically illustrated in Fig. 2. The number of defects N_D is equal to

$$N_D = 7.9\times10^{15}\int_0^{E_{max}}\alpha_{ex}dE = 7.9\times10^{15} I_\alpha, \tag{3}$$

where the integration limits extend from zero to the energy at which the exponential absorption terminates. The number of defects calculated from Eq. (3) was about 10^{16} cm^{-3}.

Modulated photocurrent is a method for depth profiling of defects in photosensitive materials [10,11]. The measurements of photocurrent and the phase shifts in frequency domain allow determination of the DOS by the use of formula [10]

$$\nu_o\sigma_c N_t(E_\omega) = \frac{2}{\pi kT}\left[\frac{f_1\mu_f e A_e\theta}{I_{ph1}(\omega)}\sin\phi - \omega\right], \tag{4}$$

where ν_o is the attempt to escape frequency, σ_c is the electron capture cross section, $N_t(E)$ is the distribution of localised states, E_ω is the energy related to frequency ω, f_1 is the excitation light amplitude, μ_f is the free carrier mobility, A_e is the electric field, I_{ph1} is the modulated photocurrent amplitude, ϕ is the phase shift.

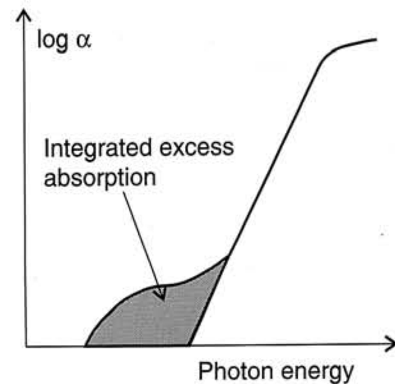

Fig. 2. Absorption spectrum of amorphous semiconductor. The number of defects is calculated from integrated excess absorption (Eq. 2). The shaded area is proportional to N_D according to (Eq. 3).

The distribution of density of states above the Fermi level obtained by MPC for a-Si:H is presented in Fig. 3. A typical peak structure for a-Si:H ascribed to $D^{0/-}$ Si dangling bond defect (Si-db) can be observed. The observed DOS values are similar to those of high quality a-Si:H films detected in other laboratories [12].

The steady state electron photoconductivity is given by

$$\sigma_{ph} = en\mu = eG\eta\mu\tau, \tag{5}$$

where η is the quantum efficiency, μ is the mobility in the conduction band, τ is the electron recombination time, G is the volume generation rate of carriers. The product

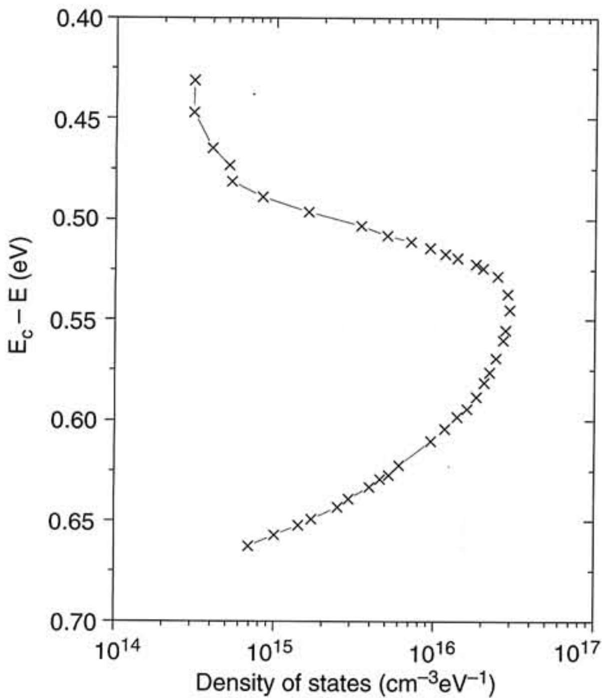

Fig. 3. The distribution of density of states above the Fermi level obtained by MPC for a-Si:H. The MPC experimental conditions: room temperature, LED 660 mn, 10^{11} photons $cm^{-2}s^{-1}$, $v = 10^7$ cms^{-1}, $\sigma_c = 10^{15}$ cm^2. Attempt to escape frequency $\nu_O = 2\times10^8$ $T^2s^{-1}K^{-2}$.

$$\eta\mu\tau = \frac{\sigma_{ph}}{eG}, \tag{6}$$

is the measure of the photoconductivity yield, also called normalised photoconductivity. The electron mobility is directly related to disorder in the amorphous structure, whereas the electron recombination time is related to the defect density in the gap through

$$t \propto 1/N_d . \tag{7}$$

The photoelectrical properties of a-Si:H were determined at the fixed photon flux of 10^{15} $cm^{-2}s^{-1}$ so as to perform the measurements at a constant hole-electron generation rate by the use of a calibrated light source AM2.0. The $\eta\mu\tau$ product was 10^{-5} cm^2/V which is also a promising result.

5. Prospects of MWCVD technique for solar cells applications

The reduction of silicon wafer thickness and low temperature process are tasks for solar cells manufacturing. Such reduction requires good surface passivation and high antireflection level. The use of silicon dioxide thin films as passivation layers traditionally needs high temperature processes. One of the good candidates as a low temperature deposited surface coating material is silicon nitride SiN_x:H which has better insulating properties than SiO_2, higher density and higher refractive index.

The MWCVD system was used for the deposition of passivation layers on various materials (quartz, silicon, stainless steel). Previous works [13,14] confirmed the possible application of nitrides and diamond like carbon films as wear resistant material for bearing balls. Also the optical properties are promising: wide bandgap and low refractive index. Some recent experiments indicated that it is possible to obtain by MWCVD silicon-nitrogen SiN_x films of tuneable band gap and refractive index. The use of microwave plasma enables a remarkable decrease in substrate temperature leading to very low temperature deposition process of materials which without a microwave plasma can be obtained only at high temperatures.

6. Conclusions

The PECVD system was used with SiH_4 to produce device quality a-Si:H which is a constituent of homojunction p-i-n and heterojunction efficient solar cells. The use of several other gases controlled by mass flow controllers allows deposition of other thin film materials such as a-C:H, a-C:N:H, SiC or a-Si:N_x:H, which are of great importance for applications in optoelectronic devices. MWCVD technology due to high microwave plasma power density can be used for low temperature deposition of nitrides and carbon layers.

Acknowledgements

The work was supported by the State Committee for Scientific Research under project 1794/112/96, Warsaw, 1996.

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