Polycrystalline silicon thin film solar cells prepared by PECVD-SPC


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1. Introduction

Nowadays approximately 95% of commercial solar cells are manufactured with crystalline silicon. The most important advantages are the maturity of the technological processes, the abundance of silicon on the surface of the earth and its lack of toxicity from the perspective of the environment. Regarding the manufacturing cost, the production of the wafers of mono- or polycrystalline silicon accounts for almost 60% of the total cost of the module, and that is the reason why the development of these or new materials is a relevant issue.

Technologies based on (mono- and polycrystalline) silicon for innovation aim at improving the conversion efficiency of cells and introducing the highest automation possible within the production process, as an alternative to lower costs and enhancing commercial viability [1].

Over the past years, there has been significant progress as to the technologies of compact photovoltaic modules, based on the thin film cells of simple and multiple juncture, deposited on transparent or metallic flexible...
substrates. Even though the global efficiencies are lower, costs due to mass production of the technologies and the significant decrease in the quantity of silicon are very promising [2–4].

This work presents preliminary results on the development of polycrystalline silicon thin film solar cells using the luminescent discharge technique of silane gas (PECVD) and its mixtures with doping gases (PH3, B2H6) for the deposition of the different layers constituting the cell. High deposition rates are reached with this method (above 2 nm/s), the material being structurally amorphous with high hydrogen content. High temperature annealing is applied in order to convert the amorphous films into polycrystalline films. The optimization of this process implies controlling the dehydrogenation of the films, the stages of crystallization (incubation, nucleation and grain growth) as a function of annealing temperatures and the structural characteristics of the amorphous material, determined by the preparation conditions at the plasma reactor. The photovoltaic devices used at this first stage are of the mesa type, with a total area of 3.14 mm².

2. Experimental

For the deposition of the different layers of the cell, our team built and used a radio frequency plasma reactor of the capacitor type. It is formed by two electrodes of 10 cm diameter and separated by a distance of 11 mm. It was placed in a high vacuum system, with a pre-chamber, a sample introduction system, shutters with different masks, radiation heater and a gas manifold system with five input valves. The gases used, silane and two 1% solutions of phosphine and the other of diborane, entered the system through mass flow meters. The operating conditions for the reactor were power: RF 8–10 W, temperature of the substrate: 150–300 °C and pressure: 600 microbar. The structure of the cells was constituted by six overlapping films, namely Antireflective (SiN), layer n+, layer p (BSF) and metallic electrodes (Al or Ag). Glass as Schott Borofloat type 33 and AF-37 were used as substrates.

Annealing was performed in a high temperature stationary furnace with temperature control source and heating ramp under inert nitrogen atmosphere. For hydrogen content, control films were deposited on high resistivity monocrystalline silicon, and the spectra of infrared absorption were measured with a Perking-Elmer spectrometer. The optical and transportation characteristics of the amorphous and crystallized deposits were determined by their UV–Vis transmittance spectra, using a Pharmacy spectrometer, conductivity measures and photoconductivity in a cryostat from 0 to 250 °C, and ambipolar length by SSPG. Crystalline structure and grain size were measured from X-ray diffraction spectra, by applying Scherrer’s formula. Crystallinity degree % was measured from the reflectance curves.

Those cells of an area of 3–4 mm² were characterized by their curves I-V and spectral response. From these, with a program developed by us, cell parameters such as Icc, Voc, FF, Rs and η% were determined.

3. Results and discussion

3.1. Dehydrogenation process

The material deposited by PECVD at 200–250 °C is amorphous and of a high hydrogen content. Each silicon atom can bond one (monohydrate) or two hydrogen atoms (dihydrate), thus completing rings of 5 and 7 atoms typical of an amorphous net. In general, concentration depends on the temperature of the substrate (8–11%). Amorphous non-hydrogenated silicon crystallizes at temperatures of over 600 °C, but hydrogen diffuses outwards visibly from silicon at 300 °C. It is known that the effusion rate of hydrogen increases with temperature, showing 400 °C maximum, which corresponds to the release of dihydrates or their conversion into monohydrates, and another at 600 °C for the effusion of monohydrates [5].

Fig. 1 shows the correlative infrared spectra of the amorphous hydrogenated silicon in which the two clear effects of annealing are exhibited. First is the decrease in intensity of the peaks as a function of temperature and annealing time. Residual hydrogen at 500 °C of 1% approximately after 10 h of annealing at 300, 400 and 500 °C can be seen. Second is the changes in the shape presented by the wide peak between 2000 and 2100 cm⁻¹, which is the addition of the stretching signal of monohydrides (peak at 2000 cm⁻¹) and the dihydrides (peak at 2100 cm⁻¹). Substituting this peak by two Gaussians centred at 2000 and 2100 cm⁻¹ it is possible to see the relative composition of mono- and dihydrates, as shown in Fig. 2.

The evolution of the peak at 2000–2100 during annealing shows that not until a temperature of 400 °C is reached, will dihydrates diffuse more rapidly than monohydrites, which do so at 500 °C.

Gradual annealing is necessary because if films are introduced directly at 500 or 600 °C, effusion is so fast, which causes hydrogen accumulation at the interface with
3.2. Crystallization of films

There are three controlling stages in the crystallization process: (a) incubation time, (b) nucleation time and (c) growth rate. They all depend on the structure of the initial material, the thermal pattern applied and they determine the final grain size of the non-hydrogenated silicon thin film [7,8]. It has been shown that for non-hydrogenated silicon the lower the deposition temperature, the higher the net disorder. In this situation the incubation and nucleation times are longer and the growth rate is predominant [8], obtaining large size grains. In our case we are limited in the deposition temperature values we can use. Below 200 °C the adhesion of the films is bad, and they start to separate from the glass during the annealing process due to the high compression stress in amorphous silicon.

The films in this work were deposited between 200 and 250 °C. They are later dehydrogenated by annealing in a stationary oven for 24 h, with an inert atmosphere at 600, 700 and 800 °C. At all these temperatures the films show a degree of crystallinity measured by ultraviolet reflectance greater than 90% [9]. The structure and grain size were measured by X-ray diffraction using Scherrer’s equation.

In Fig. 3 we can see a typical X-ray diffraction spectrum of a crystallized film. The crystals show preferential growth in the (1 1 1) plane, corresponding to 2θ = 28.4°. Applying Scherrer’s equation to this peak we obtained values between 200 and 300Å, independently of the annealing temperature. Such as grain size explains the high base of the (1 1 1) peak, due to the relative amount of material in grain boundaries and it also explains the results obtained for solar cells.

3.3. Solar cells

For the preparation of solar cells, three layers were deposited onto a transparent glass (Schott Borofloat 33 o AF-37) which has been previously covered by an antireflective coating (silicon nitride). The first layer of about 200nm thick is n+, heavily doped with phosphorus, from a 1% solution of phosphine in silane dilution. The second layer is p–, about 1500nm thick, from a diborane in silane dilution. The third and final layer is a gradual p+, form a diluted solution of 1% phosphine in silane. Once the films were crystallized, circular areas of silver or aluminium were deposited onto the n+ and p+ layers, serving as collection electrodes of 3.14 sqmm area. Dark and illuminated IV curves were obtained, and in same samples the spectral response as well was obtained.

In Fig. 4, we show the IV curve for the best cell obtained so far. It has a reasonable Voc (420 mV), but very low photocurrent (<200µA) and a low Fill Facto of 0.55. Such low values can be explained by the high series resistance due to grain size, since the grain boundary conduction is predominant over crystal.

The global conversion efficiency of this cell is 1.46%. Although this is indeed a low value, several characteristics of the cells are interesting, for instance, they do not present...
pinholes, the spatial homogeneity of the results over the whole 25 x 50 sqmm was very good and the juncture is of good quality, as can be seen by the Voc value.

4. Conclusions

A process of preparation of thin film polycrystalline silicon cells has been developed. Our results allow us to determine which stages have to be improved: agreement between temperature and dehydrogenation times with those required for the incubation of the crystalline nuclei and their growth rate is the key to obtain polycrystalline silicon apt for cells.

With an increase in grain size over 2 µm and applying processes of posthydrogenation of grain border, combined with rapid high temperature annealing, it is expected to reduce the series resistance and the volume of recombinations, which could cause a significant increase in the photocurrent, and therefore in cell efficiency. Subsequently, work should focus on optimizing cell design, different from the basic table type used, with the final goal of achieving cells of efficiencies of over 8%, values from which this technology is commercially viable.

REFERENCES


