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Nanocrystalline silicon films grown by Low Energy Plasma Enhanced Chemical Vapor Deposition for optoelectronic applications

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Abstract

This work deals with the properties of nanocrystalline silicon films, which have been grown using a Low Energy Plasma Enhanced Chemical Vapor Deposition (LEPECVD) process. This process permits to increase the intensity of the plasma discharge in the growth region and thus to achieve high growth rates while avoiding ion-induced surface damage of the deposited films. The structural, chemical, electrical and optical properties of the LEPECVD grown films were studied in detail as a function of the deposition parameters. As a result of this work we were able to show that the grown films present higher crystallinity and were obtained at higher deposition rate than with standard PECVD techniques. The electrical and structural properties indicate that the films are promising for application as an intrinsic layer in pin solar cell production. Further optimisation work is needed for optoelectronic applications.

Keywords: Nanocrystalline silicon; Crystallinity; Electrical properties; Optical properties

1. Introduction

Nanocrystalline silicon, as amorphous silicon, is normally prepared under form of thin layers on a convenient substrate by variants of the chemical vapor deposition (CVD) process. While amorphous silicon is a single phase material, nanocrystalline silicon (nc-Si:H) can be described as a bi-phasic material consisting of a dispersion of silicon nanocrystals embedded in a matrix of hydrogenated amorphous silicon (a-Si:H), whose volume fraction could be varied by selecting the proper preparation conditions. In both phases, a certain amount of hydrogen is dissolved, whose concentration depends as well on the deposition conditions.

It is known that nc-Si:H has been demonstrated to be an interesting alternative to amorphous silicon (a-Si:H) in photovoltaic (PV) applications, with a proven conversion efficiency of 10.9% in a pin-type cell configuration [1]. The nc-Si:H merit is at least in part due to its optical properties [2] which are better than those of a-Si:H and crystalline silicon (c-Si) in the solar spectrum range. Its use in photovoltaics is, however, not the unique possible technological application. It presents, in fact, also potential for optoelectronic application, considering that it could be thought also as a dispersion of silicon quantum dots in a amorphous, higher gap material, with some possible advantages with respect to a dispersion of silicon nanocrystals in a silicon oxide layer, yet as well easily integrable in a silicon chip and fully compatible with microelectronic processes. At least in principle, moreover, its optical properties might be tuned by controlling the surface rate of the chemical reaction via a proper selection of the process conditions, with interesting opportunities for the light emitting diodes technology.

In spite of these potential merits, nc-Si:H has never been used in the past as a serious alternative to traditional PV materials, in view of the too low deposition rates (around 0.1 nm/s) achieved with traditional deposition processes, as the PECVD (Plasma Enhanced Chemical Vapor Deposition) technique [3,4] or other variants of the CVD (Chemical Vapor Deposition) technique, banning nc-Si:H to useful industrial PV developments. Nor it was considered an

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alternative to nc-Si embedded in a silicon oxide matrix for optoelectronic applications.

Recently, however, it has been shown that by the use of conventional PECVD reactor operated with a convenient arrangement of the plasma parameters, deposition rates of the order of 1–3 nm/s could be obtained [5] compatible with industrial PV applications. This rate target has been also achieved in some preliminary experiments carried out by the present authors with the use of a LEPECVD system. This technique is based on a low-voltage, high-current arc discharge which has been so far very successfully applied, in terms of material quality, in the field of Si–Ge heterostructures grown epitaxially on Si [6].

The deposition rate is, however, not the primary condition to be satisfied for the use of this material for optoelectronic applications. It is in fact necessary to know the relationship among the other growth parameters such as temperature and hydrogen dilution and the properties of nanocrystalline material, as the optical and electrical properties of nc-Si:H should strongly depend on the nanocrystals size, on the ratio between the crystalline and amorphous phase volumes, on the residual hydrogen concentration in the solid mixture as well as on the extension and properties of the interface between the crystalline and amorphous phase and then, on the density of defects, as dangling and distorted bonds, at the nc-Si:H/a-Si:H interfaces and in the amorphous matrix.

These interface defects are in fact responsible for the occurrence of band tails and a mid gap band, leading to luminescence emission in the 0.8 eV range.

States at grain boundaries lower also lifetime and carrier mobility of the material [7]. Electron spin resonance (ESR) measurements suggest that bulk defect density in films is of the order of $10^{17}-5\times10^{18}$ cm^{-3} [8]. A later work of Klein et al. [9] showed that for a silane concentration of about 5% the spin density of films grown by Hot Wire Chemical Vapor Deposition (HWCVD) ranges between 10^{17} at cm^{-3} at a deposition temperature of 250 °C and 6×10^{19} at cm^{-3} at 450 °C.

The presence of the proper amounts of hydrogen in the deposited nc-Si:H is therefore a necessary condition for the passivation of defects and, then, for the optimisation of the carrier collection efficiency in solar cells.

Furthermore, the carrier mobility is influenced not only by the structure and composition of the amorphous matrix, but also by the distance among the nc-Si islands dispersed in the a-Si matrix, with conduction properties which could shift from quantum-mechanical tunnelling or thermally activated hopping to thermoionic emission, depending on the barrier width and height. The careful design of the experimental deposition conditions and the accurate determination of the factors which determine the electrical and optical properties of nc-Si:H is therefore crucial for the set-up of the deposition protocol and for the use of this material for any electro-optical applications.

We will report and discuss in this paper the results of an extensive work carried out using the LEPECVD technique in a temperature/silane concentration range typical for the growth of nanocrystalline silicon [7]. It will be shown how delicate the balance among the different deposition parameters in order to get the desired physical properties of the nc-Si:H deposited is. It will be shown also that a defective region sets up at the interface between the silicon nanocrystals and the amorphous matrix, which could be at least in part responsible of the still poor optoelectronic properties of this material.

2. Experimental

2.1. Sample preparation

nc-silicon film were grown by LPECVD technique. As the name indicates, by this process the growing layer is exposed to a dense, low-energy plasma which does not induce substantial damage by energetic ions. The dense plasma leads to a very efficient cracking of gaseous precursors, such as silane, which, together with intense bombardment of the surface by low-energy ions leads to high deposition rates and low surface state density.

Exceptional high growth rates up to 10 nm/s, have been obtained, in fact, in SiGe/Si heteroepitaxy by using this technique. Details about the LEPECVD apparatus used in these experiments are reported in a previous paper [10].

For the experiments different types of substrates were used, namely

- p-type ⟨100⟩ oriented thermally oxidized Si wafers (oxide thickness 1.6 μm) of 3 in. diameter on which a 2 μm thick zinc oxide layer was deposited, which permits to have a rear conductive layer for electrical conductivity measurements (Type I)
- fused silica substrates for optical absorption measurements (Type II)
- p-type ⟨100⟩ or ⟨111⟩ oriented, thermally oxidized Si wafers (oxide thickness 1.6 μm) of 3 in. diameter (Type III and Type IV)
- double-sided polished Si wafers for infrared absorption measurements; 3 in. of diameter (Type V).

Before nc-Si deposition, the samples were cleaned in a diluted HF (DHF) solution for 30 s. After loading into the LEPECVD system they were outgassed at 350 °C for 10 min. Subsequently, a 2 min hydrogen plasma-clean was applied at the same temperature using a gas flow of 5 sccm H_2 and an Ar flow of 50 sccm. The films were then deposited in the temperature range 400 °C–210 °C, using SiH_4 and H_2 flows leading to silane dilution ratios $d=\Phi(SiH_4)/(\Phi(SiH_4)+\Phi(H_2))$ ranging between $d=1.96\%$ and $d=5.6\%$, always well below the a-Si/nc-Si phase transition, which is expected at d values around $d=25\%$ [7]. The growth rate obtained ranged between 0.5 and 1.3 nm/s.