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Annealing effects on SiO_xN_y thin films: Optical and morphological properties

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ABSTRACT

The annealing effect on the properties of silicon oxynitride (SiO_xN_y) thin films has been investigated. The present contribution aims to study the structural and optical properties of SiO_xN_y thin films deposited by plasma enhanced chemical vapor deposition in view of their application in the field of photovoltaics. Evolution of the surface morphology and increase of the optical band gap with the thermal treatment have been determined and discussed in view of the application of the film as an emitter layer in heterojunction solar cells.

1. Introduction

During the last years, silicon oxynitride (SiO_xN_y) has been deeply investigated, due to its possible application in different fields, as well as its low-cost fabrication technologies. In fact, its relatively high refractive index ranging from 1.45 (SiO_2, where no N is present) to 4.08 (a-Si:H, total absence of both N and O) [1,2], together with low optical losses and large uniformity, make SiO_xN_y a very good candidate in photovoltaic devices, as emitter layer in Si based heterojunction solar cells and in optoelectronic devices, both as core and buffer layer in planar optical waveguides [1,3–7]. In addition, low density of surface states, high dielectric permittivity and a band gap that can range up to 9 eV varying the O/N ratio, promoted SiO_xN_y as a better oxide layer with respect to SiO_2 even in ultra thin-films transistors and nonvolatile memory devices [8–14]. Silicon-based oxynitride has received great attention also in LED application, thanks to its encouraging luminescence properties and in particular its ability in light emission in a very wide range [15].

The present manuscript aims to present a detailed characterization of silicon oxynitride thin films in view of their photovoltaic (PV) applications. Indeed, this material has been used as window layer and antireflective coating in thin film solar cells [16–18] and both SiO_x and SiO_xN_y layers might substitute nc-Si and a-Si emitter layers in silicon heterojunction solar cells, as they suffer less from parasitic absorption due to a larger band gap, while keeping high conductivity [19]. The investigation of the optical properties of such materials is therefore of great interest.

Due to coexistence of different phases and compositions upon annealing, the structure and the formation of SiO_xN_y together with the role of crystalline fraction and oxygen content in changing optical and electrical properties are still unclear. The dependence of conductivity and optical band gap from oxygen content has been investigated only recently in amorphous and annealed SiO_xN_y [2,16,20–22].

This manuscript focuses on the study of structural, morphological and optical properties of different samples of SiO_xN_y grown by Plasma Enhanced Chemical Vapor Deposition (PECVD) and annealed to increase the crystalline fraction for application in silicon heterojunction solar cells. It has been found that the concentration of N_2O as precursor gas and different annealing times affect both morphological and optical properties. The SiO_xN_y films containing nanocrystals have been obtained by thermal annealing process, which is known to be a process not fully compatible with PV technology; however high crystallinity can be also obtained by a proper choice of the deposition parameters in the PECVD growth chamber, becoming in this way fully compatible with solar cell technology.

2. Experimental details

SiO_xN_y thin films have been deposited by PECVD on FZ-Si and glass substrates. The system used is a PlasmaLab 100 from Oxford Instrument in a parallel plate configuration and the radio frequency is set at 13.56 MHz. The precursor gases used are silane (SiH_4), hydrogen (H_2),

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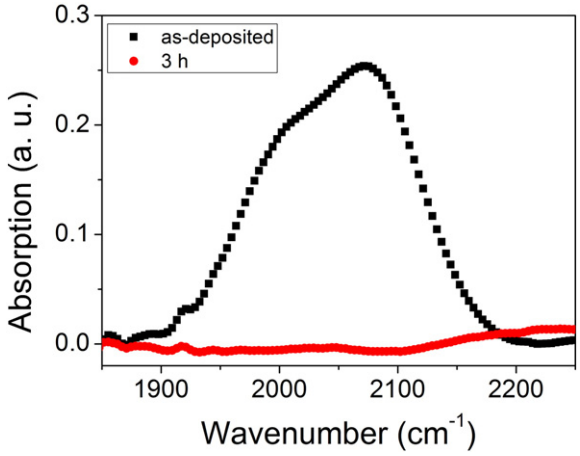

Fig. 1. FTIR spectra of the sample with $R_{N2O} = 16\%$ as-deposited (squares) and annealed for 3 h in the region 1900–220 cm^{-1}.

nitrous oxide (N_2O) and diborane (B_2H_6). The latter is diluted in hydrogen (0.5%) and in the following discussion the N_2O gas flow is referred to its dilution in silane:

$$R_{N2O} = \frac{[N_2O]}{[N_2O] + [SiH_4]} \quad (1)$$

where the square brackets indicate the gas concentrations. All the layers have been deposited at 300 °C and then subsequently annealed at 800 °C in nitrogen atmosphere to increase the crystallized fraction. Hydrogen is present in the as-deposited layers, while it desorbs during the annealing [23]. Fig. 1 shows the Fourier Transform Infra-Red (FTIR) spectra of a sample deposited at $R_{N2O} = 16\%$ in the region of Si—H_x bond (1900–2200 cm^{-1}), showing that the signal related to this bond is not present after annealing. Moreover, no peak related to N—H and O—H bonds is observed in the region 3300–3900 cm^{-1} (not shown). Please note that all the layers have been named SiO_xN_y for sake of clarity.

The silicon crystallized fraction χ is defined as:

$$\chi = \frac{I_C}{I_C + I_A} \quad (2)$$

where I_C is the integrated area of the Raman peak at 520 cm^{-1} related to the crystallized Si content of the layer, while I_A is the integrated area of the Raman peak at 480 cm^{-1} related to the amorphous Si phase [24–26]. Eq. (2) is used to compare the Si crystallized fraction of different samples. The excitation wavelength of the laser used is 488 nm.

The surface morphology of the thin films has been measured using Atomic Force Microscopy (AFM) with a Park NX10 system in non-contact mode. The tips used feature a super-sharp apex, with a curvature radius less than 5 nm (Nanosensors SSS-NCHR). The map size used for the analysis is $1 \times 1\ \mu m^2$ with a resolution of 512×512 px. The investigation of surface morphology is of great interest, as it affects the growth of subsequent layers and the performances of the final device, as evidenced by studies on thin film silicon solar cells [27].

The height–height correlation function (HHCF) has been evaluated from the AFM maps and fitted in the hypothesis of self-affine surfaces using the following expression:

$$HHCF(r) = 2R_{HHCF}^2 \left\{ 1 - \exp\left[-\left(\frac{r}{\xi} \right)^{2\alpha} \right] \right\} \quad (3)$$

with r the lateral distance between two points, R_{HHCF} the surface roughness, α the Hurst exponent and ξ the lateral correlation length. ξ represents the length scale beyond which the heights of two points of the surface are no more correlated and the Hurst exponent is a measure of the local roughness of the structures present on the surface [28,29]. The Equivalent Disk Radius (EDR) of the structures present on the layer surface has been obtained from AFM maps superimposing a segmentation mask obtained using the software Gwyddion [30]. The features present on the sample surfaces are grain-like and will be called grains in the following discussion. A filtering of the obtained mask is necessary to remove incorrectly identified grains [31], so that grains with area less than 4 px and minimum height value less than the minimum height + 1 nm are removed from the analysis.

The optical band gap E_{Tauc} has been evaluated using reflection ($R(h\nu)$) and transmission ($T(h\nu)$) spectra measured in the range 300–1500 nm obtained using a Cary spectrometer from Varian. The absorption coefficient $\alpha(h\nu)$ has been evaluated by:

$$\alpha(h\nu) = \frac{1}{d} \ln\left(\frac{1 - R(h\nu)}{T(h\nu)} \right) \quad (4)$$

where d is the thickness of the film obtained from ellipsometry measurements. Eq. (4) has been used to reduce the contribution of interference fringes, which are observed in the measured spectra [32,33]. The value of E_{Tauc} has been deduced in the hypothesis of a disordered material from a linear fit of the Tauc plot obtained following [34]:

$$(\alpha(h\nu) \cdot h\nu)^{1/2} \propto (h\nu - E_{Tauc}). \quad (5)$$

The optical analysis has been performed on the layers deposited on glass.

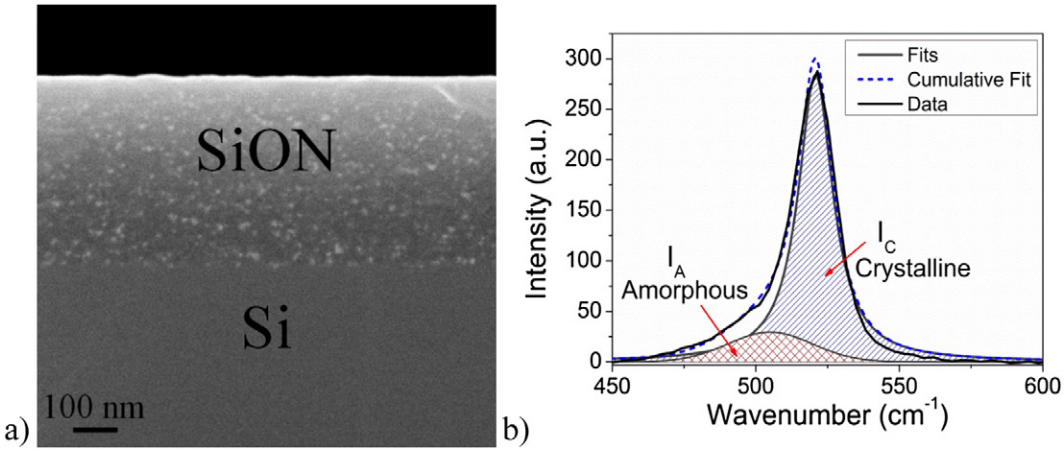

Fig. 2. SEM image (a) and Raman spectrum (b) of a SiO_xN_y layer deposited with $R_{N2O} = 16\%$, 3 h annealed.

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