



Improved thermoelectric properties of nanocrystalline hydrogenated silicon thin films by post-deposition thermal annealing



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ABSTRACT

The influence of post-deposition thermal annealing on the thermoelectric properties of n- and p-type nanocrystalline hydrogenated silicon thin films, deposited by plasma enhanced chemical vapour deposition, was studied in this work. The Power Factor of p-type films was improved from 7×10^{-5} to 4×10^{-4} W/(m.K²) as the annealing temperature, under vacuum, increased up to 400 °C while for n-type films it has a minor influence. Optimized Seebeck coefficient values of 460 μV/K and -320 μV/K were achieved for p- and n-type films, respectively, with crystalline size in the range of 10 nm, leading to remarkable low thermal conductivity values (< 10 W.m⁻¹.K⁻¹) at room temperature.

1. Introduction

Nanocrystalline hydrogenated silicon (nc-Si:H) has been investigated and developed with the purpose of enhancing the efficiency of thin film solar cells [1,2]. In addition to solar cells, a broad range of applications were also demonstrated for these materials including thin film transistors [3], sensors [3], biomedical devices [4], etc. While plasma enhanced chemical vapour deposition (PECVD) [5] is commonly used for the production of thin film solar cells, laser crystallization of a-Si:H [6] and thermal annealing [7] processes have also been demonstrated in literature. Regarding thermoelectric (TE) energy conversion, crystalline silicon is known by its high Seebeck coefficient (S) values but also high thermal conductivity (k). This is a major drawback to maximize its efficiency, which can be compared among materials through the Figure of Merit value (ZT, Eq. (1)), since ideal TE materials need to combine high electrical conductivity (σ) and Seebeck coefficient with low thermal conductivity: $ZT = \frac{S^2 \sigma}{k} \cdot T$.

Recently, significant reduction in the thermal conductivity of silicon-based materials [8,9] has been achieved through nanometer scale grain sizes, approaching the values of the most efficient TE materials BiTe based alloys [10,11]. In previous work, we have reported the thermoelectric properties of both p-type and n-type nc-Si:H thin films (TF), with optimized deposition parameters, and applications to a small TE module as proof of concept [12], but more research can be found in literature related to nanocrystalline silicon thin films with optimized TE

properties [13,14]. In this paper we report nc-Si:H TF with improved Seebeck coefficient and Power Factor (PF = S² × σ) values, comparable to those seen in bulk nanocrystalline silicon produced by sintering [15]. The enhancement of the TE properties of both p- and n-type nc-Si:H films was obtained by post-deposition annealing process.

2. Experimental details

The n- and p-type nc-Si:H samples were produced by PECVD with the optimized conditions described in the previous study [12]. After the deposition, they were submitted to different annealing temperatures (T_A): 170, 250, 300 and 400 °C, during 2 h in vacuum (10⁻⁵ mbar). The influence of T_A on the films properties was studied by several different techniques. Scanning electron microscope (Zeiss Auriga) was used to analyze the surface morphology. Spectroscopic Ellipsometry (SE) was used to analyze the percentage of the crystalline (X_c) and amorphous (X_a) phases, the presence of voids (X_{voids}) and the films thickness (160 nm ± 5 nm for n-type and 110 nm ± 5 nm for p-type) [5,16]. The crystallinity was further confirmed by Raman spectra [17].

Thermal conductivity measurements were conducted using time domain thermoreflectance (TDTR) [18,19], an optical pump-probe experiment which utilizes a train of ultrashort laser pulses to induce a modulated heating event on the surface of the sample. For these TDTR measurements, samples were coated with thin metal films, which act as a transducer to relate the absorbed pump energy to the temporal

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temperature change on the surface of the sample via the thermoreflectance change monitored in the time domain. The specific TDTR system used is centered around a sub-picosecond Ti:Sapph oscillator. Pump pulses at 8.8 MHz were sinusoidally modulated using an electro-optic modulator, and the thermoreflectance decay monitored from this pump heating event with a time delayed probe pulse offering up to 6.5 ns of pump-probe delay. An 80 ± 5 nm Al transducer has been deposited on the thin film stack, and the thickness of this transducer was validated with picosecond acoustic analysis [20,21]. The analysis of this data, described in detail elsewhere [18,19] involves least squares fitting to determine through plane thermal resistances in the system with highest sensitivity to the dominant thermal resistors, in this case the nano crystalline Si layer. Literature values have been assumed for the heat capacity and thermal conductivity of the Al [22] and Si [23,24] correcting for the measured porosity in the nano crystalline region of the sample [25]. Using laser spot sizes of 48 μm and 12 μm diameters for the pump and probe, respectively, assures that the thermal transport monitored via TDTR is a fully uniform column, and therefore nearly one dimensional in the through-plane direction [19]. Electrical and thermoelectrical characterizations were performed in a home-made setup [26], where a thermal gradient (ΔT) is created, parallel to the substrate, by placing the sample between two Peltier modules, TEC1-12707, each connected to an independent power source. ΔT is monitored through a thermal image taken with a FLIRA310 thermal camera. The thermovoltage (ΔV) is measured using a nano-voltmeter (Agilent 34420A) while keeping the average temperature constant at RT. For the materials' Seebeck coefficient determination, ΔV is measured in open circuit conditions, while for device output power characterization ($P_{\text{out}} = I_{\text{out}} \times V_{\text{out}}$), a variable load resistance is connected to the TE elements and the ΔV is measured through its terminals, from short-circuit to open-circuit conditions. Three different TE devices were fabricated: two devices with 2 n-p pairs (with as deposited films and post deposition annealing at 250 °C) and a third device only with n-type elements, 4 legs (annealed at 250 °C). The TE legs were patterned using mechanical masks during their deposition and were interconnected with Al evaporated paths (250 nm thick, ohmic), ending with a geometry of 2 mm long by 4 mm wide (dimension between metallic pads).

3. Results

The influence of the T_A on σ and S values, for both p-type and n-type, are shown in the Fig. 1. Since T_A of 250 °C corresponds to the value that optimizes the thermoelectric properties of both p- and n-type films, Fig. 1 also includes the scanning electron microscopy (SEM) images of samples before and after the annealing step.

By combining both σ and S values, it is possible to calculate the total PF and its dependence with the T_A . Fig. 2 shows a clear optimization of the PF values for T_A around 250 °C.

SE results were modelled as described in previous papers to analyze the influence of T_A on the crystalline (X_c) and amorphous (X_a) fractions of bulk material and surface one, as shown in Fig. 3a) and b).

The crystallinity was further confirmed by Raman spectra (depicted in Fig. 4a), and small grain sizes were estimated for both types of films from XRD (Fig. 4b). The ratio between the area of the peaks related to nanocrystalline and/or grain boundaries (nc/gb-Si) at $\approx 500 \text{ cm}^{-1}$ and the ones associated with crystalline silicon (c-Si) at $\approx 520 \text{ cm}^{-1}$ has been evaluated before and after annealing. The mean grain size was estimated by the deviation of the transverse optical peak (TO) mode relatively to that of c-Si (520 cm^{-1}): $d_{\text{Raman}} = 2\pi \sqrt{\text{B} / \Delta\omega}$, where B is 2 nm^2 and $\Delta\omega$ the deviation to the c-Si peak [27], giving a $d = 5.6 \text{ nm}$ (n-type) and $d = 4.8 \text{ nm}$ (p-type) before annealing and slightly decreases to 4.8 nm (n-type) and 4.6 nm (p-type) after annealing.

The low grain sizes of these materials are expected to contribute to low k , which is fundamental to have high ZT values. The measured k values of the annealed films (250 °C) are $7.9 \pm 2.7 \text{ W/(m.K)}$, for the n-

type films, and $5.2 \pm 0.8 \text{ W/(m.K)}$ for the p-type films, which are comparable to the values of nanowires or bulk nanocrystalline silicon from nanopowders [11].

To use both types of nc-Si:H samples to build TE devices, the maximum output power generated by a n-p TE pair occurs when the load resistance equals the total n-p pair resistance (according to Eq. (1)).

$$P_{\text{max}} = \frac{(S_n + S_p)^2 \Delta T^2}{4(R_n + R_p)} \quad (1)$$

To confirm the influence of the annealing on a TE device's voltage, power and current, three different TE devices were fabricated and characterized: two with n-p nc-Si pairs (as deposited and annealed at 250 °C, Fig. 5a) and a third device using only n-type elements (annealed at 250 °C, Fig. 5b). Their output Voltage/Power vs Current curves were measured when applying a $\Delta T = 8 \text{ °C}$ (Fig. 5c).

4. Discussion

From Fig. 1 it is visible that the T_A increases up to 250 °C leads to σ enhancement from 4.6×10^2 to $2.2 \times 10^3 (\Omega\text{m})^{-1}$ and S decrease from 400 to 370 $\mu\text{V/K}$ on the p-type samples. A further T_A increase inverts this tendency and a small drop of σ is observed while S augment up to 460 $\mu\text{V/K}$. When comparing to p-type films, T_A has minor effect on n-type samples both for σ and S , however, for T_A between 250 and 300 °C S reaches a maximum of $-324 \mu\text{V/K}$ (at 250 °C) and σ of $1.0 \times 10^4 (\Omega\text{m})^{-1}$ (at 300 °C). The SEM image of the as-deposited p-type samples shows some grains surrounded by amorphous tissue, while after annealing at 250 °C apparently, the grains get more uniform, with less amorphous regions. The SEM images of n-type samples reveal uniform grains after annealing without evident change in amorphous tissue.

Due to the dependency of the PF with σ and the square of S , it is visible in Fig. 2 that it increases from $7.5 \times 10^{-5} \text{ W/(m.K}^2)$, without annealing, to $3\text{--}4 \times 10^{-4} \text{ W/(m.K}^2)$, for p-type samples, and reaches values around $10^{-3} \text{ W/(m.K}^2)$ for n-type films, after annealing in vacuum, with the pair reaching a maximum at 250 °C.

From the SE analysis, it was possible to infer that the increase of T_A enhances $X_a\%$, from 1 to 15%, corresponding to a reduction of bulk $X_c\%$, from 95 to 80%, meaning that the percentage of voids kept unchanged. Regarding the surface, X_c is lower than it was on bulk, varying between 45% and 60%, while the amorphous fraction at the surface almost disappears with the increase of T_A . This behaviour agrees with SEM images where the surface morphology appears to be more crystalline at $T_A = 250 \text{ °C}$, as mentioned before. These variations on the bulk X_a and X_c are responsible for the observed optimization of σ and S , meaning that equilibrium between X_a and X_c is required to simultaneously optimize these parameters. High degree of crystallinity enhances conductivity and grain boundaries contribute to S increase due to low energy electrons filtering [28].

The crystallinity was further confirmed by Raman spectra, showing that the percentage of nc/gb-Si has changed from 46% and 64% (for n- and p-type films, respectively) to 45% and 54% with the annealing at 250 °C, confirming the crystalline fraction enhancement. As shown in Fig. 4), the peak related to amorphous silicon (a-Si) is almost absent for both films and the intensity of the crystalline peak has decreased with the annealing step, which agrees with the SE results.

Grain boundary phonon scattering is the expected mechanism driving the low k values. When comparing the measured k values of the annealed films, at 250 °C ($k_n = 7.9 \pm 2.7 \text{ W/(m.K)}$ and $k_p = 5.2 \pm 0.8 \text{ W/(m.K)}$) with the as deposited ones, ($k_n = 3.3 \pm 0.7 \text{ W/(m.K)}$ and $k_p = 2.7 \pm 0.4 \text{ W/(m.K)}$) [12] a small increase of the k values with the annealing is observed. This is most likely due to the decrease of phonon-boundary scattering corresponding to the increase in the nc/crystalline fraction. In these films, k is limited

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