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Deposition and characterization of polymorphous germanium films prepared by low frequency PECVD

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ABSTRACT

In this work we have deposited polymorphous germanium (pm-Ge:H) thin films by low frequency plasma enhanced chemical vapor deposition (LF-PECVD). We have studied the effect of the deposition pressure on the structural and electric characteristics of the films. Atomic force microscopy was used to analyze the surface roughness of the pm-Ge:H films, while transmission electron microscopy was used to observe the cross section.
The temperature dependence of conductivity ($\sigma(T)$), deposition rate (V_d), activation energy (E_a) and the temperature coefficient of resistance (TCR) were extracted on the pm-Ge:H films deposited at different pressure values. An optimal pressure range was found, in order to produce pm-Ge:H films with high E_a and TCR which are key parameters for thermal detection applications.

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) and germanium (a-Ge:H) are standard materials in the microelectronics and photovoltaic industries. They are compatible with Silicon CMOS technology, are deposited at low substrate temperatures ($T_s = 200$ °C) by plasma enhanced chemical vapor deposition (PECVD) and have a direct optical band gap (E_g). These features make them excellent materials for optoelectronic devices, solar cells [1] and thermal detectors [2]. However, amorphous materials have also drawbacks, as a large density of states in the band gap, poor transport properties and poor stability [3].

It has been demonstrated that by modifying the deposition parameters of amorphous materials (using PECVD) it is possible to form nanocrystals of diameters of above 2–5 nm in the amorphous matrix; such materials are known as polymorphous semiconductors [4,5]. The presence of the nanocrystals distributed in the amorphous matrix reduces the density of states, improving the transport properties and stability of the films [3]. Besides the above, polymorphous materials preserve the characteristics of amorphous semiconductors, which are a direct optical band gap and large activation energy (E_a).

Therefore polymorphous semiconductors are excellent materials for the fabrication of more stable devices, as thermal detectors and solar cells. For instance the use of pm-Si:H in thin film solar cells with efficiencies higher than 8%, and more stable against light soaking, than those employing a-Si:H films has been reported [6].

Even that pm-Si:H and pm-Ge:H have been studied for solar cells applications [6,7], at present there is no work related to the study of these films as thermo-sensing elements in infrared detectors (un cooled microbolometers).

For thermal detection applications, a-Si:H is very attractive, due to its very large activation energy ($E_a = 0.8$–1 eV) and very high temperature coefficient of resistance, TCR ($\alpha(T) = 0.1$–0.12 K^{-1}), related to E_a with the expression ($\alpha(T) = -E_a/kT^2$). However a-Si:H has a very high undesirable resistivity, which causes a mismatch with the input impedance of the read-out circuits.

In the most developed IR detector arrays boron doping is employed in order to reduce the high resistance of a-Si:H [2]. The boron doped a-Si:H (a-Si:H,B) films have an improved σ_{RT}; however, it also has a reduced E_a (~0.22 eV) and TCR (~0.028 K^{-1}). Coupled with the above, a-Si:H,B is not a very stable material and suffers of degradation with time.

In our previous work we have studied a-Ge:H and a-SiGe:H films [8–10] as thermo sensing elements for thermal detectors (un-cooled microbolometers) and we have demonstrated that this material has advantages over a-Si:H,B since it has a larger E_a (~0.34 eV) and TCR (~0.046 K^{-1}) with a moderated σ_{RT} (6×10^{-5}).

In this work we present our results on the deposition and characterization of pm-Ge:H thin films produced by low frequency (LF) PECVD from a GeH_4/H_2 gas mixture. We have studied the effect of the deposition pressure, on the structural and electrical characteristics

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of the films, aiming to improve the characteristics that are important for IR detection, as E_a, TCR and σ_{RT}.

2. Experimental

A series of pm-Ge:H films was deposited in a capacitively coupled low frequency PECVD reactor, working at 110 KHz, with an RF power density of 90 mW/cm^2. The films were deposited at a substrate temperature of 200 °C, from a GeH_4/H_2 gas mixture, with gas flow rates of GeH_4 = 50 sccm and H_2 = 1000 sccm, at a different pressure values: 600, 1000, 1500, 2000 and 2500 mTorr.

Atomic force microscopy (AFM, Nanosurf EasyScan 2.3) was used to study the surface roughness of the pm-Ge:H films aiming to observe the effect of the deposition pressure on the formation of germanium clusters on the film surface.

A pm-Ge:H film was selected and its cross section was analyzed in the search of nanocrystals. For that purpose transmission electron microscopy (TEM, JEM-2200FS) was used and the film was prepared using a focused ion beam (FIB) and the lift-out technique [11].

A set of films was deposited on corning glass containing titanium contacts for electrical characterization. The samples were placed in a vacuum thermostat at pressure of 30 mTorr and measurements of temperature dependence of conductivity ($\sigma(T)$) in the range of 300–400 K were performed in order to obtain the activation energy (E_a), the temperature coefficient of resistance (TCR) and the room temperature conductivity (σ_{RT}). An electrometer (model 6517-A, Keithley Inst.) was used for $I(U)$ measurements and a temperature controller (model K-20, MMR Inst.) was used for the films temperature setting.

For characterization of responsivity with infrared radiation, a set of pm-Ge:H films deposited on corning glass was prepared using photolithography and RIE etching to define film patterns of area of $70 \times 66\ \mu m^2$ and using e-beam evaporation titanium contacts were deposited over them.

The samples were placed in a vacuum thermostat at 30 mTorr, at room temperature and $I(U)$ characteristics were measured in the films in dark and under IR radiation. The source of IR radiation was a SiC globar source, which provides an intensity (I_0) of 5.3×10^{-2} Wcm^{-2}. A zinc selenide window (ZnSe), which has a transmission of 70% in the wavelength range of 0.6–20 μm was used as a filter for IR radiation.

A voltage was applied to the films and the current was measured with an electrometer. The current responsivity (R_I) was calculated as $R_I = \Delta I / P_{in}$, where ΔI is the increment in current from dark (I_D) to IR radiation (I_{IR}), $\Delta I = I_{IR} - I_D$. P_{in} is the incident power ($P_{in} = 2.47 \times 10^{-6}$ W), calculated as $P_{in} = I_0 {}^{*} A_{cell}$, where I_0 is the IR source intensity and A_{cell} is the sample area.

From the experimental data the voltage responsivity ($R_u = \Delta U / P_{in}$) was extracted, where ΔU is the increment of voltage from dark to IR radiation for a fixed value of current.

3. Results

As was discussed on Experimental section, AFM was used to analyze the surface roughness of the pm-Ge:H films. Fig. 1 shows 3-D AFM images ($2 \times 2\ \mu m^2$) of five surfaces of pm-Ge:H film deposited over corning glass at different pressure values. The average surface roughness $<S_a>$ of the films was calculated by a statistic analysis from a $2 \times 2\ \mu m^2$ scanned area [12].

The films that had a lower $<S_a>$ were those deposited at lower and higher pressures (600 and 2500 mTorr), with $<S_a>$ of 1.01 and 1.04 nm, respectively. In turn, the films that had a larger $<S_a>$ were those deposited at pressure values of 1000, 1500 and 2000 mTorr with $<S_a>$ of 1.8, 1.5 and 1.3 nm, respectively.

Fig. 2 shows a cross section obtained by TEM, of a selected pm-Ge:H film deposited at 2000 mTorr over corning glass. As was discussed on experimental part, a very thin slice of an a-Ge:H film was extracted

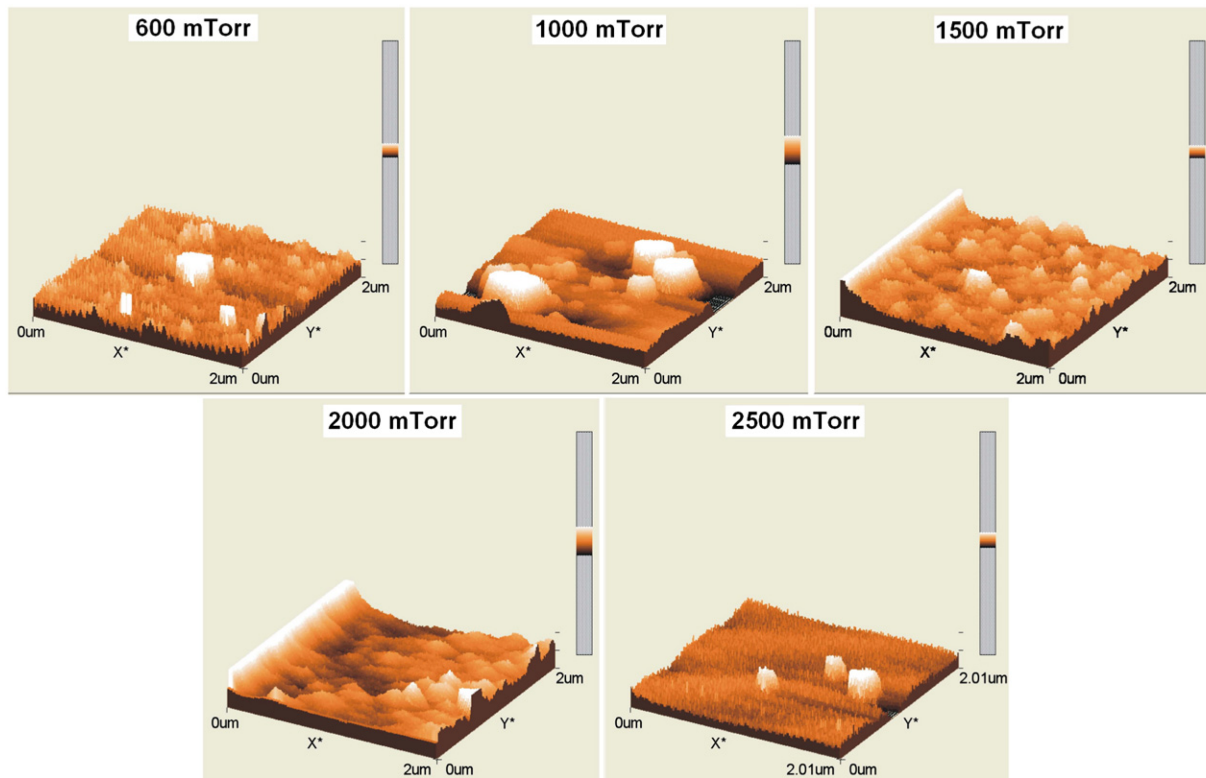

Fig. 1. Atomic force microscopy (AFM) images of a series of pm-Ge:H films deposited at different pressure values.

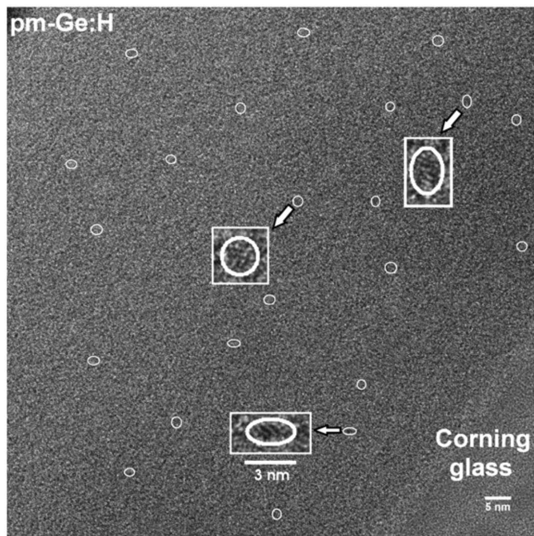

Fig. 2. Cross section of a pm-Ge:H film obtained by TEM.

using a FIB and the lift-out technique. In the TEM picture several nanocrystals of about 2–4 nm are appreciated.

Fig. 3 shows the dependence of the room temperature conductivity (σ_{RT}) of the pm-Ge:H films as a function of the deposition pressure. As one can see, the σ_{RT} decreases as the deposition pressure increases. The measured σ_{RT} was in the range of 2×10^{-5}–8×10^{-4} $(\Omega\ \text{cm})^{-1}$. In Fig. 3 the dependence of the deposition rate (V_d) with the deposition pressure is also observed. At low deposition pressure (600 mTorr) V_d is of above 1.1 Å/s and increases to 1.6 Å/s at higher deposition pressure (1000 mTorr). A further increment in pressure results in a decrement on V_d. At a deposition pressure of 2500 mTorr, the calculated V_d is of above 0.2 Å/s.

Measurements of temperature dependence of conductivity ($\sigma(T)$) in the range of 300–400 K were performed in the series of pm-Ge:H films and are shown as inset in Fig. 4. The E_a values were obtained in the different films as the slope of the linear fit of the Arrhenius curve Ln(σ) vs. 1/KT. The error values obtained by the linear fit were very low, below ±0.01% in all the films. Since E_a is proportional to the TCR according to the relationship $\text{TCR} = -E_a/kT^2$, the TCR values calculated have an error below 0.1%.

Fig. 4 shows E_a and TCR of the pm-Ge:H films as a function of the deposition pressure. The measured E_a of the pm-Ge:H films is in the range of 0.29–0.39 eV, while the TCR is in the range of 0.037–0.05 K^{-1} (or 3.7–5% K^{-1}).

From $I(U)$ measurements in dark and under IR radiation on the pm-Ge:H films of area of $70\times66\ \mu m^2$ the current and voltage responsivity were calculated, as was discussed on Experimental section.

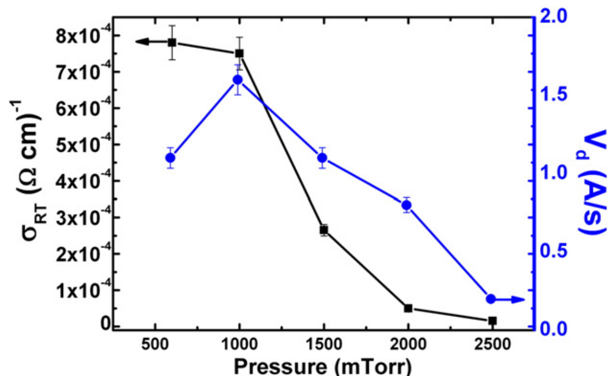

Fig. 3. Room temperature conductivity and deposition rate of pm-Ge:H films as a function of the deposition pressure.

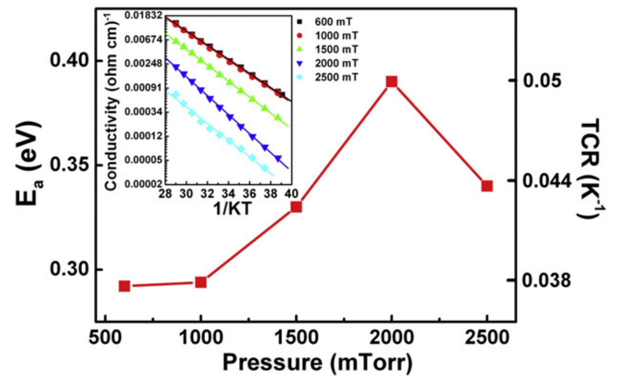

Fig. 4. Activation energy and TCR of pm-Ge:H films as a function of the deposition pressure.

Fig. 5 shows the deposition pressure dependence of R_I, where it is observed that the film deposited at 1000 mTorr has the larger R_I (1.3×10^{-2} A/W) and it decreases significantly in the films deposited at higher pressure.

Since R_I is too sensitive to the conductivity of the films, it is more suitable to use R_u to determine and compare the performance of the thermo-sensing films. In Fig. 5 is observed that R_u is in the range of 2.1×10^5–3.4×10^5 U/W for a wide range of deposition pressure values (600–2500 mTorr). The larger R_u (3.4×10^5 V/W) is observed in the film deposited at 1500 mTorr.

4. Discussion

From the analysis of the AFM images of the surface of the pm-Ge:H films showed in Fig. 1, we observe that at low deposition pressure (600 mTorr), the film surface has some clusters, and for larger deposition pressures (1000–2000 mTorr), the clusters formed in the films surface are of larger size (height and width). However, for larger deposition pressure (2500 mTorr) the clusters decrease in size again, that was corroborated with the average surface roughness <S_a> statistical analysis [12], where the films deposited at pressures of 1000–2000 mTorr have larger <S_a> values.

The presence of clusters in the film surface is possibly related to the presence of nanocrystals on the amorphous matrix. In Fig. 2 the cross section of a selected pm-Ge:H film deposited at 2000 mTorr, where some nanocrystals are marked, is shown. The presence of these nanocrystals is an indication of the polymorphous nature of the films deposited.

In order to confirm the nature of the films, electrical characterization was performed, where E_a and TCR were extracted. These values

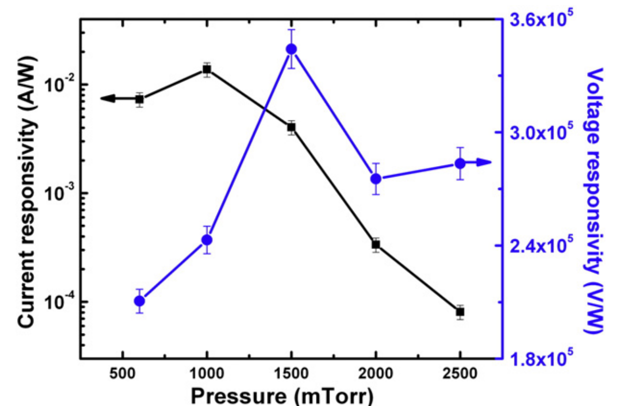

Fig. 5. Current and voltage responsivity of pm-Ge:H films as a function of the deposition pressure.

are similar than those reported for a-Ge:H [9,10] as is expected, since the presence of nanocrystals in the amorphous matrix does not have a strong effect on the properties of the amorphous materials (as E_a or E_g), but makes them much more stable, with better transport properties as larger electron mobility (μ_e).

In our previous work, pm-Si:H films were studied [15], and it was observed that an increment on the deposition pressure resulted on an increment on the films σ_{RT}. That behavior is possibly related to the fact that larger deposition pressure stimulates the formation of nanocrystals during the pm-Si:H films deposition [13]. The presence of nanocrystals in the amorphous matrix reduces the density of states, improving the electrical properties of the film (as μ_e and likely σ_{RT}).

However in this work a decrement of σ_{RT} of the pm-Ge:H films as the deposition pressure increases is observed. An explanation of the above behavior is quite complicated, since several factors could be responsible. For instance, oxygen contamination on pm-Ge:H deposition could be the reason, since oxygen acts as impurity on pm-Ge:H films [7].

The decrement of the deposition rate (V_d) of pm-Ge:H films when deposition pressure increases, also is consequence of the formation of nanocrystals on the amorphous matrix, since high deposition pressures (>1000 mTorr) stimulate the formation of nanocrystals in SiH_4/H_2 plasmas; however very high pressures (~4000 mTorr) lead to the formation of powder in the chamber [13], reducing significantly the material being deposited and resulting on a reduction of the film thickness and V_d. Even that it has been demonstrated in SiH_4/H_2 plasmas, the same concept can be applicable to GeH_4/H_2 plasmas.

From the temperature dependence of conductivity, E_a and TCR were extracted in the films. The larger values were obtained in films deposited at 2000 mTorr, E_a (0.39 eV) and TCR (0.05 k^{-1}). These values are higher than those reported for a-Si:H,B (E_a = 0.22 eV, TCR = 0.028 k^{-1}), material used as thermo-sensing films in commercial microbolometers [2,14] and also for a-Ge:H and a-SiGe:H (E_a = 0.34 eV, TCR = 0.046 k^{-1}) [7–10].

Finally, from responsivity characterization performed in pm-Ge:H films, we obtained large R_u values (~3.4×10^5 V/W), which are close to those reported for a-Si:H,B (1×10^6 U/W) [2] and a-SiGe:H (7×10^5 U/W) [9]. Moreover, it is important to point out that the films reported in the present work were directly deposited on corning glass, while in the refereed works the films are supported by microbridges. The latter provides a much more efficient thermal isolation, resulting in an increment on the films responsivity.

5. Conclusions

In this work, we have deposited and characterized pm-Ge:H films prepared by low frequency (LF) PECVD, aiming to use them as thermo-sensing elements on IR detectors. The deposition pressure was varied in order to observe its effect on the film characteristics that are important for IR detection, as E_a, TCR, σ_{RT} and responsivity with IR radiation.

Our results indicate that there is an optimum range of pressure (1000–2000 mTorr) in order to produce films with larger E_a, TCR, and R_u, maintaining a moderated σ_{RT}. Moreover, E_a values of 0.39 eV with a TCR of above 0.05 K^{-1} and R_u of 3.4×10^5 V/W were measured in pm-Ge:H films deposited on corning glass.

Finally, we can conclude that pm-Ge:H is a promising material to be used as thermo-sensing film in un-cooled microbolometers, due to its advantages over a-Si:H,B and the better stability demonstrated in this kind of films.

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