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Short communication

Study of polymorphous silicon as thermo-sensing film for infrared detectors

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ABSTRACT

In this work we have deposited and characterized pm-Si:H thin films obtained by plasma deposition. Our aim is to use pm-Si:H as thermo-sensing element for infrared (IR) detectors based on un-cooled microbolometers. We have studied the electrical characteristics of pm-Si:H that are figures of merit important for IR detection, as activation energy, thermal coefficient of resistance (TCR), room temperature conductivity (σ_{RT}) and responsivity under IR radiation. The influence of the substrate temperature (200 °C and 300 °C) on the pm-Si:H characteristics has been also studied. Our results shown that pm-Si:H is an excellent candidate to be used as thermo-sensing film for microbolometers, due to its large activation energy and TCR, with an improved σ_{RT}.

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1. Introduction

Currently, there is a renewed interest in the development of low cost and high reliability night vision systems based on large arrays of thermal detectors (un-cooled microbolometer arrays). This arises as a consequence of the incorporation of the low-temperature deposited thermo-sensing materials and the surface micro-machining technology to the silicon CMOS fabrication process [1–4]. The operation of a microbolometer is based on the temperature rise of its thermo-sensing material by the absorption of the incident IR radiation. The temperature rise causes a change on its electrical resistance, which in turn is measured by an external circuit. The main requirements for the thermo-sensing material for a resistive microbolometer are among others, a high activation energy value (E_a), which is related to the temperature coefficient of resistance, TCR ($\alpha(T)$), through $\alpha(T) = -E_a/kT^2$. Therefore a high E_a value will result in a large TCR. In addition to the aforementioned, the material must have a moderated room temperature conductivity value (σ_{RT}), and also must be compatible with the standard silicon CMOS technology.

Hydrogenated amorphous silicon (a-Si:H) prepared by plasma enhanced chemical vapor deposition (PECVD) is a mature material in the microelectronics and photovoltaic industries and has been adopted as thermo-sensing film for commercial un-cooled microbolometers [1–5]. Moreover a-Si:H is compatible with the silicon CMOS technology, has a very high activation energy, $E_a \approx 0.8$–1 eV and, consequently, a high TCR, $\alpha(T) \approx 0.1$–0.12 K^{-1}, however, it also has an undesirable high resistivity value, which produces a mismatch between the microbolometer and the input impedance of the read-out integrated circuits (ROICs). In order to reduce the high resistance of a-Si:H films, boron doping has been proposed as a solution for reducing the high resistance of the devices. The boron doped a-Si:H films resulted with an improved σ_{RT}, but also showed a reduced E_a (~0.22 eV) and TCR (0.028 K^{-1}) [5]. It is also pertinent to mention that a-Si:H has a large density of states in the band gap, which results in a poor transport properties and low stability of the material [6,7].

In this respect, we propose polymorphous silicon (pm-Si:H) as a serious candidate for replacing a-Si:H as thermo sensing film in microbolometers. Basically pm-Si:H is formed of an amorphous silicon matrix with nanocrystals (of about 2–3 nm) distributed through the material. The presence of nanocrystals impacts the properties of the material by reducing the density of states and improving the transport properties and stability of the films [6–9]. It is important to note that intrinsic pm-Si:H still preserving the characteristics of a-Si:H, such as a direct optical band gap (~1.6–1.8 eV), and large E_a and TCR. In our previous work [10] we demonstrated that it is possible to produce pm-Si:H films using a PECVD system working at low frequency (~110 kHz), despite of a larger ion bombardment that occurs in this type of reactors.

On the other hand, we have demonstrated microbolometers in which the thermo-sensing film is sandwiched between two metal electrodes, instead of the standard configuration where metal

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Table 1
Deposition conditions of four series of pm-Si:H films, where the deposition pressure, substrate temperature and SiH_4/H_2 flow rates have been varied.

	Film number	Pressure mTorr	Temperature °C	SiH_4 flow sccm	H_2 flow sccm
Series 1	1 2 3	1500 2000 2500	300	50	1000
Series 2	4 5 6	1500 2000 2500	300	150	3000
Series 3	7 8 9	1500 2000 2500	200	50	1000
Series 4	10 11 12	1500 2000 2500	200	150	3000

electrodes make contact with the thermo-sensing film in the same plane at the edge of the film. This device configuration, that we have named sandwich structure, has demonstrated a reduction on the cell resistance in about three orders of magnitude [11,12]. Therefore, this device configuration may be very useful for using thermo-sensing layers with the largest TCR without an excessive increasing in the resistance of the device.

In this work we show our results on the deposition and characterization of pm-Si:H films produced by low frequency (LF) PECVD from SiH_4 and H_2 mixtures. We have studied systematically the effect of the deposition parameters as substrate temperature, deposition pressure and gas flow rates, on the electrical characteristics of pm-Si:H, aiming to improve the characteristics that are important for IR detection, as E_a, TCR, σ_{RT} and responsivity with IR radiation.

2. Experimental

The pm-Si:H films were deposited in a capacitively coupled low frequency PECVD reactor, in which we set the operating RF frequency at 110 kHz. The films were deposited from a SiH_4/H_2 mixture, with a RF power density of 90 mW/cm^2. For the deposition of pm-Si:H, are necessary both, a large pressure value in the range of 1000–2000 mTorr and large H_2/SiH_4 ratios (around 20/1) [6–9]. The films were deposited at the pressure values of 1500, 2000 and 2500 mTorr, at two substrate temperatures 300 °C and 200 °C. Two gas flow rates SiH_4 = 50 sccm/H_2 = 1000 sccm and SiH_4 = 150 sccm/H_2 = 3000 sccm were used in this work. Table 1 shows the deposition conditions of pm-Si:H films produced.

Transmission electron microscopy (HRTEM, JEM-2200FS) was used to study the bulk transversal structure of pm-Si:H films deposited on (1 0 0) c-Si. X-ray diffraction (XRD) was performed in pm-Si:H films deposited on corning glass. A μc-Si:H film was also used for reference, in order to compare its spectra with those of the pm-Si:H films. The electrical characterization was performed in a vacuum thermostat at a pressure of 30 mTorr. We used an electrometer (model 6517-A, Keithley Inst.) for the $I(U)$ measurements and a temperature controller (model K-20, MMR Inst.) for the films temperature control. In order to obtain the activation energy (E_a), the temperature coefficient of resistance (TCR) and the room temperature conductivity (σ_{RT}) of the pm-Si:H films, measurements of temperature dependence of conductivity ($\sigma(T)$) in the range of 300–400 K were performed. For that purpose pm-Si:H films were deposited on corning glass containing 10-mm-long titanium stripes, with separation of 2 mm.

For responsivity measurements pm-Si:H films were deposited on corning glass and by photolithography followed by RIE etching film patterns of 70 μm × 66 μm were defined. Titanium contacts were deposited by e-beam evaporation on the top of the films, with a separation of 40 μm. $I(U)$ measurements were performed in the aforementioned samples in dark conditions and under IR illumination. The IR source used was a silicon carbide (SiC) globar source, which has an intensity of $I_0 = 5.3 \times 10^{-2}$ W/cm^2 with an IR spectrum from 1 to 20 μm [11,12]. The samples were placed in the

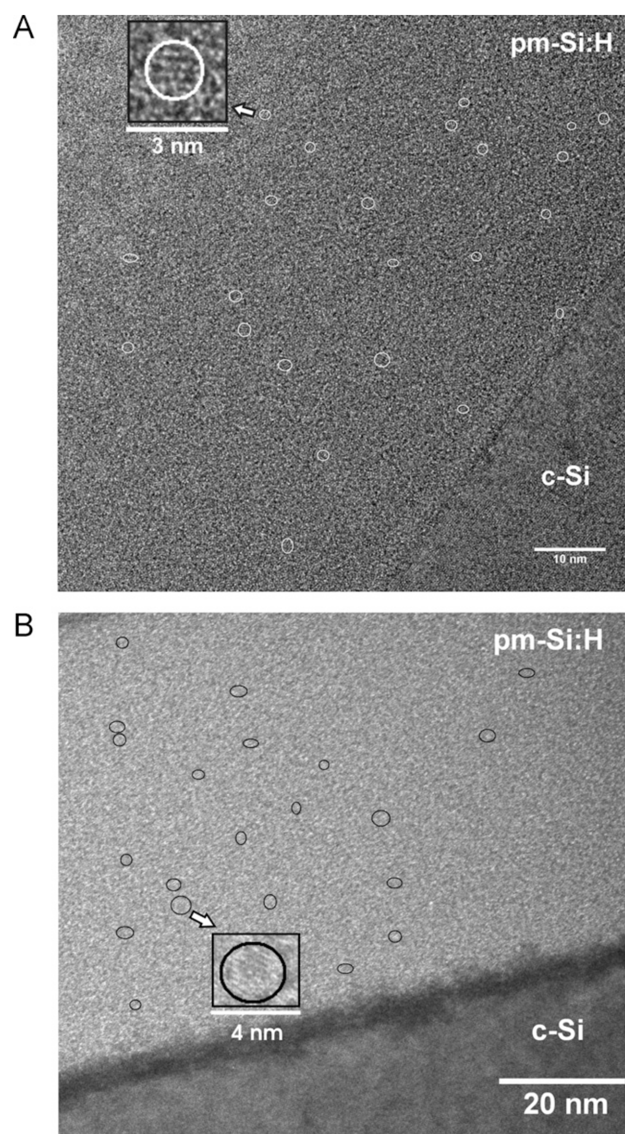

Fig. 1. Transversal view of pm-Si:H films obtained by HRTEM: (A) pm-Si:H film deposited at 300 °C and (B) pm-Si:H film deposited at 200 °C.

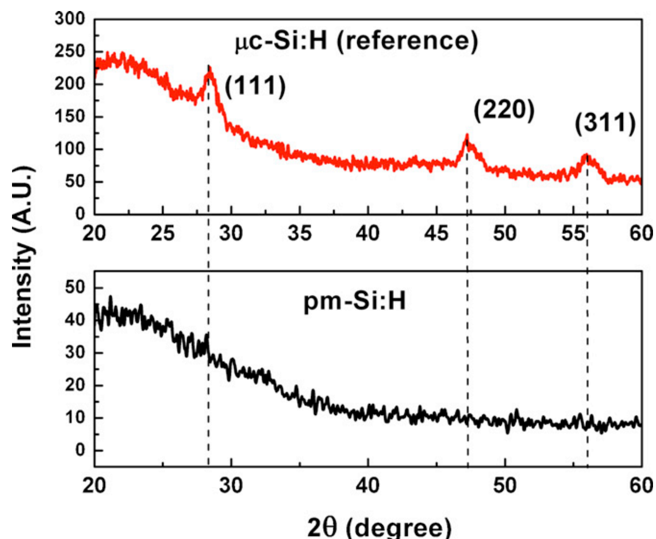

Fig. 2. XRD spectra of a pm-Si:H film compared with a μc-Si:H film (used as reference).

vacuum thermostat mentioned above, at room temperature and illuminated through a zinc selenide (ZnSe) window, which has a 70% transmission in the range of 0.6–20 μm.

The responsivity is defined as the ratio of the pixel (detector) output signal to the incident radiant power (in Watts). The output signal is an electrical signal that can be voltage or current, thus R can be expressed in Volts/Watts (voltage responsivity, R_U) or Amps/Watts (current responsivity, R_I) [13]. We measured R_I from $I(U)$ measurements using Eq. (1), where ΔI is the increment in current from dark (I_D) to IR illumination (I_{IR}) condition, $\Delta I = I_{IR} - I_D$, and P_{in} is the incident power. P_{in} is obtained from $P_{in} = I_0 \times A_{cell}$, where I_0 is the lamp intensity and A_{cell} is the sample area. Therefore the measured incident power $P_{in} = 1.7 \times 10^{-6}$ W after to passing through the ZnSe window.

$$R_I = \frac{\Delta I}{P_{in}} \quad (1)$$

3. Results and discussion

Fig. 1 shows the cross section obtained by HRTEM, of two selected pm-Si:H films, which were deposited at a gas flow rate ratio of SiH_4 = 150 sccm/H_2 = 3000 sccm and pressure of 2000 mTorr, for two substrate temperatures (A) 300 °C and (B) 200 °C, respectively. In this figure, several nanocrystals of size about 2–3 nm are circled and the insert in each micrograph shows an enlargement of a single nanocrystal. This is an indication of the polymorphous nature of the deposited films.

As was mentioned in Section 2, XRD characterization was performed on the deposited pm-Si:H films for knowing more about the nature of the nanocrystals. Fig. 2 shows a comparison of the X-ray diffraction spectra of a μc-Si:H film used as reference and that of a typical pm-Si:H film. The X-ray diffraction spectra of a μc-Si:H film has sharp peaks related to (1 1 1), (2 2 0) and (3 1 1) crystallographic planes, which confirms the crystalline nature of these film. However, the X-ray diffraction spectra of the pm-Si:H film do not show any peaks. This may be caused by either: the nanocrystals are of very small size (2–3 nm in average) or they are too few and scattered along the amorphous matrix. Therefore the dominant signal is that of the amorphous phase and, for the time been, we could

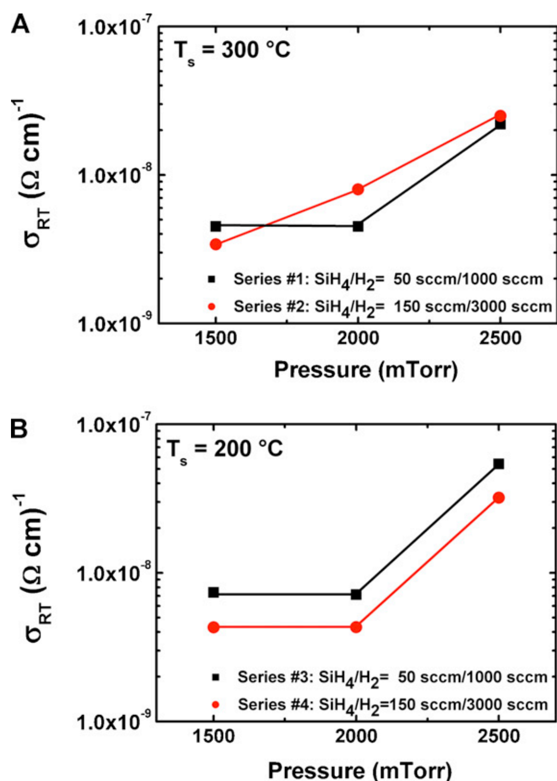

Fig. 3. Room temperature conductivity of polymorphous films as a function of the deposition pressure: (A) Series 1 and 2 deposited at T_s of 300 °C and (B) Series 3 and 4 deposited at T_s of 200 °C.

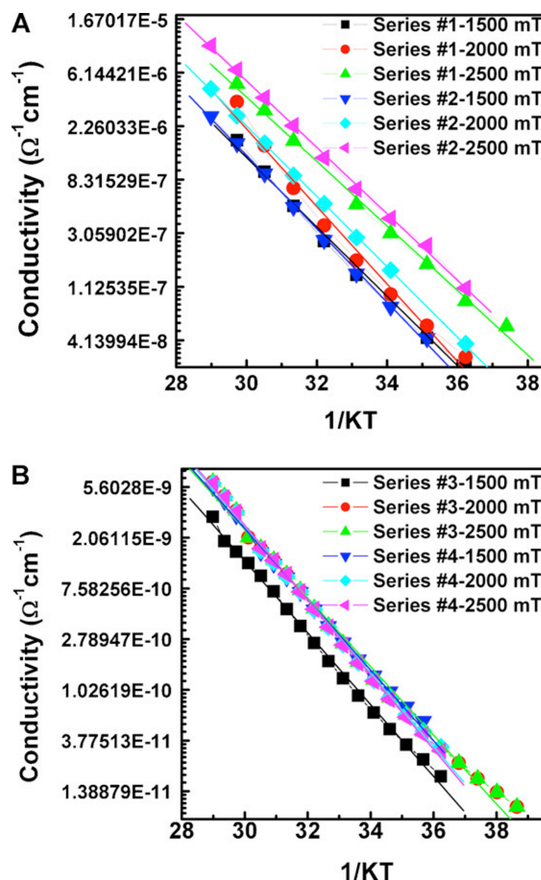

Fig. 4. Temperature dependence of conductivity: (A) Series 1 and 2 deposited at T_s of 300 °C and (B) Series 3 and 4 deposited at T_s of 200 °C.

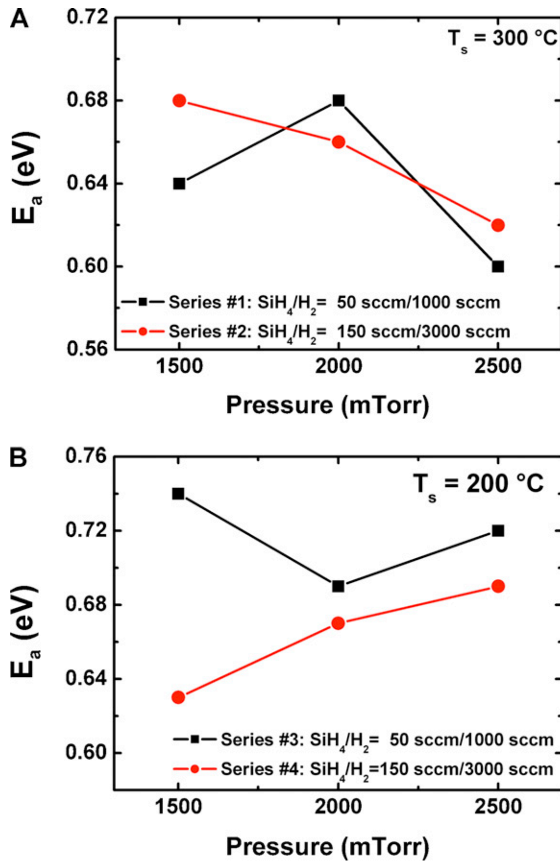

Fig. 5. Activation energy of polymorphous films as a function of the deposition pressure: (A) Series 1 and 2 deposited at T_s of 300 °C and (B) Series 3 and 4 deposited at T_s of 200 °C.

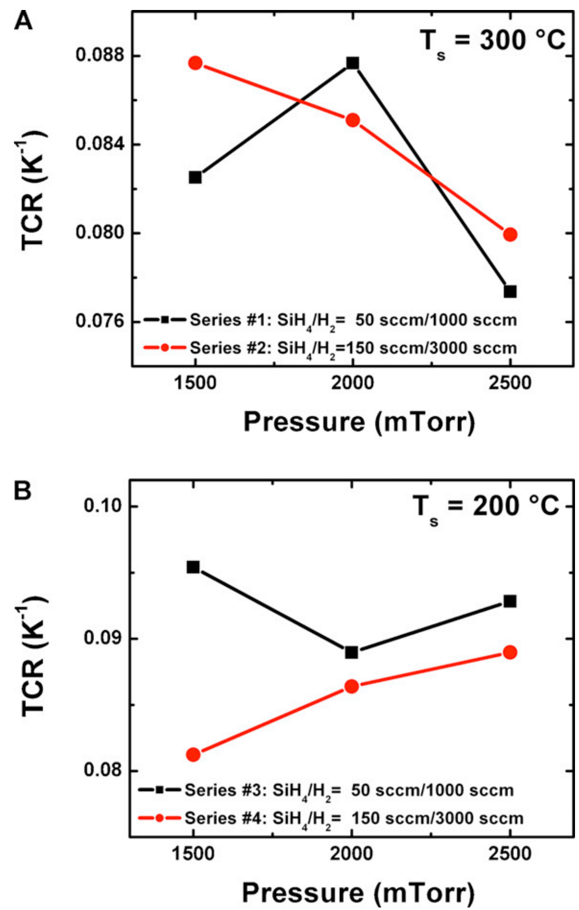

Fig. 6. TCR of polymorphous films as a function of the deposition pressure: (A) Series 1 and 2 deposited at T_s of 300 °C and (B) Series 3 and 4 deposited at T_s of 200 °C.

not demonstrate a correlation of the XRD spectra with the HRTEM observations.

Fig. 3 shows the measured values of σ_{RT} of the pm-Si:H films as resulted from the change in deposition pressure. The σ_{RT} was measured for the two gas flow rates used for the films deposition (SiH_4 = 50 sccm/H_2 = 1000 sccm and SiH_4 = 150 sccm/H_2 = 3000 sccm) and for two substrate temperatures, 300 °C (Fig. 3A) and 200 °C (Fig. 3B). In Fig. 3 a general trend is observed, the σ_{RT} value increases with the deposition pressure. It is pertinent to note that the σ_{RT} measured at the larger deposition pressure (2500 mTorr) is of about two orders of magnitude larger than that of the intrinsic hydrogenated amorphous silicon (a-si:H), deposited at low pressure (100–600 mTorr) which typical σ_{RT} is around $1 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$ [14]. This result is consistent the presence of nanocrystals because large deposition pressures stimulates the formation of nanocrystals in SiH_4/H_2 plasmas during the pm-Si:H films deposition [15]. On the other hand, it is generally accepted that hydrogenated amorphous silicon has a large density of states. When nanocrystals are produced and incorporated in the amorphous matrix, the density of defects is reduced, since the atoms that form the nanocrystals do not have dangling bonds. As a consequence, the density of states is reduced (to below $10^{15}\ cm^{-3}$). A reduction on the density of defects and states will result in a lower scattering of electrons, and larger time between collisions. In fact it has been demonstrated that electrons in pm-Si:H have larger mobility values than electrons in a-Si:H [7]. Therefore an improvement in the room temperature conductivity is observed as the deposition pressure is increased and nanocrystals are incorporated to the amorphous matrix.

From measurements of temperature dependence of conductivity ($\sigma(T)$) in the range of 300–400 K, we extracted the activation energy (E_a) for the four series of the deposited pm-Si:H films as is shown in Fig. 4(A) and (B). Fig. 5 shows the dependence of E_a with the deposition pressure, for two gas flow rates and for two substrate temperatures, 300 °C in Fig. 5A and 200 °C in Fig. 5B. From those results we cannot find a clear dependence of E_a with the deposition pressure. However, we observed a general trend, the larger E_a values in the pm-Si:H films are found in films deposited at

Table 2
Performance characteristics of the pm-si:H films produced in this work, compared with intrinsic a-Si:H, a-SiGe:H and boron doped a-Si:H (a-Si:H,B).

	Pressure mTorr	Temp. °C	SiH_4 flow sccm	H_2 flow sccm	R_I A/W	R_U V/W	E_a eV	TCR K^{-1}	σ_{RT} $(\Omega\,cm)^{-1}$
Series 1	2000	300	50	1000	2.7×10^{-7}	1.2×10^{6}	0.68	0.087	2.2×10^{-8}
Series 2		300	150	3000	8.2×10^{-7}	4.7×10^{6}	0.67	0.085	2.5×10^{-8}
Series 3		200	50	1000	4.9×10^{-7}	1.7×10^{6}	0.74	0.095	6×10^{-8}
Series 4		200	150	3000	6.5×10^{-7}	3.5×10^{6}	0.69	0.088	3.2×10^{-8}
a-Si:H [14]	600	300	–	No	–	–	0.86	0.11	1×10^{-9}
a-SiGe:H [16]	600	300	25 (GeH_4 = 25)	1000	2×10^{-3}	7.2×10^{5}	0.36	0.046	2×10^{-5}
a-Si:H,B [5]	–	–	–	–	–	1×10^{6}	0.22	0.028	–

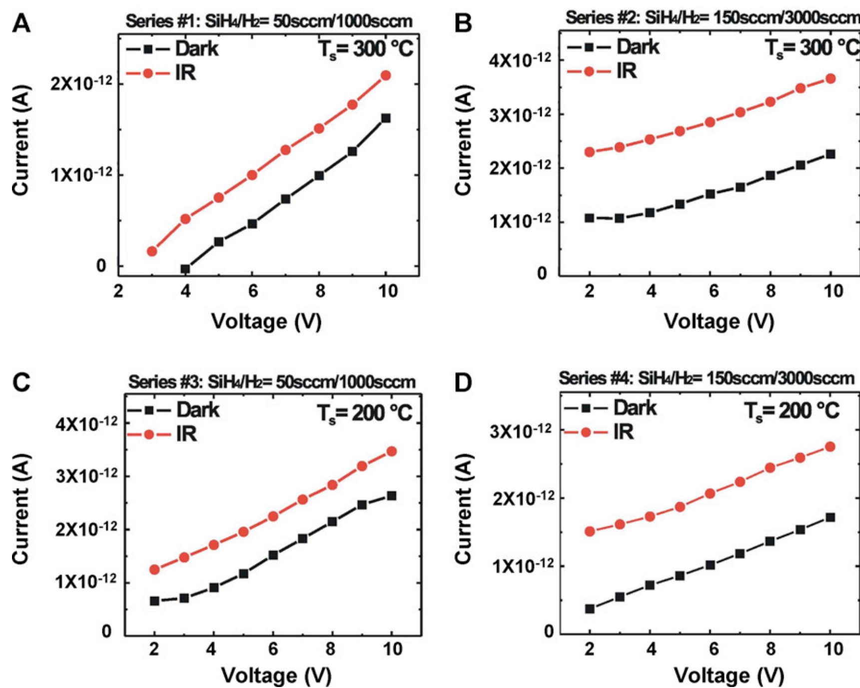

Fig. 7. *I*(*U*) characteristics in dark and under IR radiation of four pm-Si:H films deposited at 2000 mTorr, belonging to: (A) Series 1: $T_s = 300\,^{\circ}$C and $SiH_4 = 50$ sccm/$H_2 = 1000$ sccm, (B) Series 2: $T_s = 300\,^{\circ}$C and $SiH_4 = 150$ sccm/$H_2 = 3000$ sccm, (C) Series 3: $T_s = 200\,^{\circ}$C and $SiH_4 = 50$ sccm/$H_2 = 1000$ sccm, and (D) Series 4: $T_s = 200\,^{\circ}$C and $SiH_4 = 150$ sccm/$H_2 = 3000$ sccm.

the lower substrate temperature (200 °C) for lower gas flow rates ($SiH_4 = 50$ sccm/$H_2 = 1000$ sccm).

Despite the large E_a values obtained in the pm-Si:H films (as large as 0.74 eV), these values are still smaller to those of intrinsic a-Si:H films (0.8–1 eV) [5,14]. The possible reason is the fact that our PECVD reactor consists of a single chamber, which is usually used for the deposition of intrinsic and doped materials. Even though an extensively cleaning was performed before each film deposition, it is possible that some contamination remained on the chamber walls, reducing slightly the values of E_a.

The temperature coefficient of resistance (TCR) was calculated from E_a as mentioned in the experimental part. Fig. 6(A) and (B) shows the dependence of the TCR with the deposition pressure for the four series of pm-Si:H films (Table 1). As in the case of E_a, there is not a clear dependence of the TCR with the deposition pressure. However, we observe that larger TCR values were obtained in pm-Si:H films deposited at lower substrate temperature (200 °C). The largest value of TCR obtained was of around 0.095 K^{-1} (or 9.5%K^{-1}), which is close to that of intrinsic a-Si:H (~0.11 K^{-1}).

In reference to the responsivity of the films, we performed *I*(*U*) measurements in dark and under IR radiation on some selected pm-Si:H films of area of 70 μm × 66 μm. The selected films were those deposited at 2000 mTorr belonging to each of the four film series (Table 1). Those films were analyzed by HRTEM and therefore we are sure that there are nanocrystals on them. Fig. 7(A)–(D) shows the *I*(*U*) characteristics in dark and under IR radiation of four prepared samples. As we can observe in the figures, a significant increment from dark to IR radiation (ΔI) is observed in all the films. The calculated ΔI is in the range of 30–50%. The calculated the current responsivity (R_I), which is shown in Table 2, where also is included the voltage responsivity (R_U) extracted from the data of Fig. 7 and the values of E_a, TCR and σ_{RT} obtained for each series. For comparison, in Table 2 also are characteristic figures of merit of intrinsic a-Si:H [14] and a-SiGe:H [16] films deposited in the same PECVD reactor for comparison, as well, are included some values of boron doped a-Si:H (a-Si:H,B) [5], material which is currently used as thermo-sensing element in commercial arrays of un-cooled microbolometers.

As one can see, the TCR of pm-Si:H is close to that of intrinsic a-Si:H, with the advantage of larger σ_{RT} in almost two orders of magnitude. When is compared with a-Si:H,B, pm-Si:H has a larger TCR (in more than three times), however, its σ_{RT} is lower in about 3 orders of magnitude. Therefore, even though an improvement on the characteristics in pm-Si:H have been achieved, the σ_{RT} is still an issue.

4. Conclusions

In this work, we deposited and characterized four series of pm-Si:H films prepared by low frequency (LF) PECVD. Our aim is to use pm-Si:H as thermo-sensing element on IR detectors. The deposition parameters (substrate temperature, gas flow rates and pressure) were varied in order to observe their effect on the film characteristics that are important for IR detection, as E_a, TCR and σ_{RT}.

Our results indicate that lower substrates temperatures result on films with larger TCR, while high deposition pressure results on an increment of the σ_{RT} in the films produced. The increment on σ_{RT} is related to the fact that at larger deposition pressure the formation of nanocrystals in the SiH_4/H_2 plasmas is stimulated, and the presence of a large density of nanocrystals in the pm-Si:H films improve the electrical characteristics, as the electron mobility and σ_{RT}.

Finally, we can conclude that pm-Si:H is a promising material to be used as thermo-sensing film in un-cooled microbolometers, due to its advantages over a-Si:H.

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