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# Study of polymorphous silicon and germanium as thermo-sensing films for infrared detectors

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ABSTRACT

In this work we present a comparative study on the electrical characteristics of polymorphous silicon (pm-Si:H) and polymorphous germanium (pm-Ge:H) thin films deposited by low frequency plasma enhanced chemical vapor deposition (LF-PECVD), aiming to use them as thermo sensing elements in un-cooled microbolometers.
We studied the effect of the deposition pressure on the film characteristics that are important for IR detection, as the activation energy ($E_a$), the thermal coefficient of resistance (TCR), the room temperature conductivity ($\sigma_{RT}$) and the film responsivity with IR radiation.
Our results indicate that polymorphous films have advantages over boron doped a-Si:H, material which is currently employed as thermo-sensing element in commercial microbolometer arrays.
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## 1. Introduction

Nowadays, there is a significant development on the fabrication of very large thermal detector arrays, as a consequence of incorporating the low-temperature surface micro-machining technology on the standard silicon CMOS process [1,2].

The basic unit (pixel) used on the most developed (and commercially available) thermal detector arrays is the microbolometer. Basically it is a temperature dependent resistor, which contains an IR absorbing film deposited on a thermo-sensing element. Those films are supported by a microbridge structure, which provides thermal isolation.

The operation of a microbolometer is based on the increment of the thermo-sensing film temperature due to the absorption of incident IR radiation, resulting on a change of the electrical resistance, which is measured by an external circuit.

For high performance microbolometers, the thermo-sensing materials should satisfy the following requirements: high activation energy ($E_a$), high temperature coefficient of resistance, TCR ($\alpha(T)$), moderated room temperature conductivity ($\sigma_{RT}$), and compatibility with standard CMOS fabrication technology.

Hydrogenated amorphous silicon (a-Si:H) deposited by plasma enhanced chemical vapor deposition (PECVD) is very attractive to be used as thermo-sensing film in un-cooled microbolometers [1–4] because of its very high activation energy ($E_a \approx 0.8$–1 eV), very high TCR ($\alpha(T) \approx 0.1$–0.12 $K^{-1}$) and its compatibility with the standard silicon CMOS technology. However, it also has very high resistivity ($>10^9$ Ω cm), which results in a mismatch with the input impedance of the read-out circuits [4].

In commercial microbolometer arrays, boron doped a-Si:H (a-Si:H,B) has been adopted as thermo sensing film, due to its improved $\sigma_{RT}$ in several orders of magnitude, when it is compared with intrinsic a-Si:H. However a-Si:H,B also has a reduced $E_a$ (~0.22 eV) and TCR (~0.028 $K^{-1}$), which is traduced in low film sensitivity to IR radiation.

In our previous work [5,6] we have studied hydrogenated amorphous silicon–germanium (a-$Ge_xSi_y$:H) and hydrogenated germanium (a-Ge:H) thin films for thermal detection applications, and have demonstrated that those materials are very suitable to be used as thermo-sensing elements in microbolometers. Those films have a relatively large $E_a$, of above 0.34 eV, providing a TCR of 0.046 $K^{-1}$ and improved $\sigma_{RT}$ in four orders of magnitude, when it is compared with a-Si:H. However, despite of the improvement of the electrical properties of intrinsic a-$Ge_xSi_y$:H and a-Ge:H films, the $\sigma_{RT}$ and stability of those films are still issues.

Recently, it has been demonstrated that by modifying the conditions in the deposition of hydrogenated amorphous materials by PECVD, it is possible to produce nanocrystals (of above 2–5 nm) distributed in the amorphous matrix; such materials are known as polymorphous semiconductors. The nanocrystals in the amorphous matrix reduce the density of states and improve the electric properties and stability of the

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films [7–10]. In this aspect we believe that polymorphous semiconductors (pm-Si:H and pm-Ge:H) are serious candidates to replace a-Si:H,B as thermo sensing film in commercial microbolometers.

In our previous work [11] 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.

In this work we have deposited by Low Frequency (LF) PECVD pm-Si:H and pm-Ge:H thin films from $SiH_4/H_2$ and $GeH_4/H_2$ gas mixtures, respectively. We have studied the effect of the deposition pressure, on the electrical characteristics of the films that are important for IR detection, as $E_a$, TCR, $\sigma_{RT}$ and responsivity with IR radiation.

## 2. Experimental

Two series of polymorphous films were deposited in a capacitively coupled low frequency PECVD reactor, working at 110 kHz, with a RF power density of 90 mW/cm$^2$, at a substrate temperature ($T_s$) of 200 °C and at different pressure values (1500, 2000 and 2500 mTorr). A series labeled as #1 consisted of pm-Si:H films deposited from a $SiH_4/H_2$ gas mixture, at gas flow rates of $SiH_4$ = 50 sccm and $H_2$ = 1000 sccm; while a series labeled as #2 consisted of pm-Ge:H films deposited from a $GeH_4/H_2$ gas mixture, at gas flow rates of $GeH_4$ = 50 sccm and $H_2$ = 1000 sccm.

High Resolution Transmission Electron Microscopy (HRTEM, JEM-2200FS) was used to analyze the bulk cross section of polymorphous films aiming to observe the presence of nanocrystals in the amorphous matrix. The polymorphous films were prepared for TEM characterization using a Focused Ion Beam (FIB) and the lift-out technique [12].

Measurements of temperature dependence of conductivity ($\sigma(T)$) were performed in pm-Si:H and pm-Ge:H films deposited on corning glass containing titanium stripes in order to obtain the activation energy ($E_a$), the temperature coefficient of resistance (TCR) and the room temperature conductivity ($\sigma_{RT}$).

For the above characterization, the samples were placed in a vacuum thermostat at a pressure of 30 mTorr. A temperature controller (model K-20, MMR Inst.) was used to set the temperature in the films (in the range of 300–400 K) and an electrometer (model 6517-A, Keithley Inst.) was used to obtain current–voltage characteristics (I(U)) of the films at different temperature values.

For responsivity characterization we selected two films of each series (pm-Si:H and pm-Ge:H) deposited on corning glass at 2000 mTorr. The films were specially prepared using photolithography and RIE etching to define film patterns of $70\times66\ \mu m^2$ and using e-beam evaporation, titanium contacts were deposited over the films. The samples were placed in a vacuum thermostat with a zinc selenide window (ZnSe), which has a transmission of 70% in the wavelength range of 0.6–20 μm.

I(U) characteristics were measured in the samples in dark and under IR radiation at a pressure of 30 mTorr, at room temperature. The source of IR radiation is a SiC globar source, which provides an intensity ($I_0$) of $5.3\times10^{-2}$ W cm$^{-2}$. A voltage in the range of 2–10 V 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 $\Delta I$ 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 ($2.47\times10^{-6}$ W), calculated as $P_{in} = I_0 * A_{cell}$, where $I_0$ is the IR source intensity and $A_{cell}$ is the sample area.

## 3. Results

As was discussed in the Experimental section, TEM characterization was performed in the polymorphous films in order to observe the presence of nanocrystals in the amorphous matrix. Fig. 1 shows two cross sections of polymorphous films deposited at a pressure of 2000 mTorr. Fig. 1A corresponds to a pm-Si:H film, while Fig. 1B corresponds to a pm-Ge:H film. As one can observe both films contain several nanocrystals with diameter of above 2–4 nm.

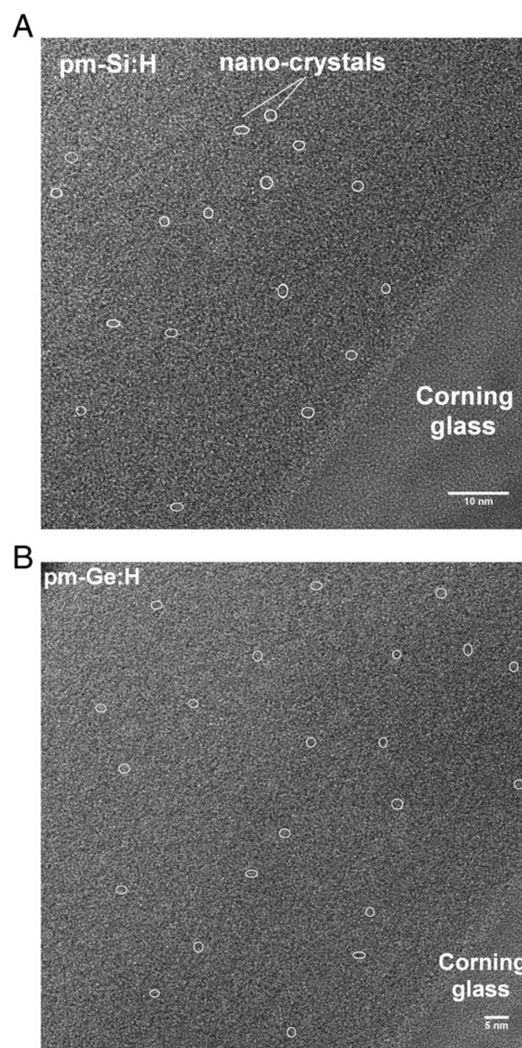


**Fig. 1.** Cross section of polymorphous films obtained by HRTEM. A) pm-Si:H and B) pm-Ge:H.

Fig. 2 shows the deposition rate ($V_d$) as a function of the deposition pressure of both series of polymorphous films (series #1: pm-Si:H and series #2: pm-Ge:H). From the figure it is evident that the deposition rate of pm-Ge:H is larger than that of pm-Si:H in almost two times. Since the deposition parameters were the same for both

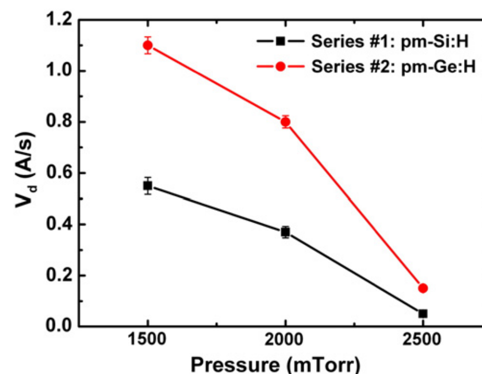


**Fig. 2.** Deposition rate of polymorphous films as a function of the deposition pressure: series #1: pm-Si:H and series #2: pm-Ge:H.

series, the above result indicates that the dissociation of $GeH_4$ is more efficient than that of $SiH_4$.

Fig. 3 shows the deposition pressure dependence of the polymorphous films' room temperature conductivity ($\sigma_{RT}$), where it is shown that $\sigma_{RT}$ of pm-Si:H is in the range of $8\times10^{-9}$–$6\times10^{-8}$ $(\Omega\ \text{cm})^{-1}$, while $\sigma_{RT}$ of pm-Ge:H is in the range of $2\times10^{-5}$–$2\times10^{-4}$ $(\Omega\ \text{cm})^{-1}$. A difference in conductivity of above four orders of magnitude is observed between the two types of films.

From measurements of temperature dependence of conductivity ($\sigma(T)$) in the range of 300–400 K, we extracted the activation energy ($E_a$) and calculated the TCR in the pm-Si:H and pm-Ge:H series. The activation energy ($E_a$) values were obtained in the different films as the slope of the linear fit of the Arrhenius curve Ln($\sigma$) vs 1/KT. The error values obtained by the linear fit were very low, below +/−0.01% in all the samples.

Since $E_a$ is proportional to the TCR according to the relationship $TCR = -E_a/kT^2$, where k is the Boltzmann constant, expressed in eV and T is the temperature expressed in K, it is also clear that the TCR values calculated have errors below 0.1%.

Fig. 4 shows the deposition pressure dependence of $E_a$ and TCR of both series of polymorphous films (series #1: pm-Si:H and series #2: pm-Ge:H). The measured $E_a$ of pm-Si:H is in the range of 0.68–0.73 eV, while for pm-Ge:H it is in the range of 0.32–0.39 eV. As one can see, the $E_a$ values of pm-Si:H are more than two times larger than those of pm-Ge:H. The largest value of TCR for pm-Si:H is 0.095 $K^{-1}$ (or 9.5%$K^{-1}$), while for pm-Ge:H it is 0.05 $K^{-1}$ (or 5%$K^{-1}$).

Finally, as was discussed in the Experimental part, I(U) characteristics in dark and under IR radiation were measured on two selected polymorphous films of area of $70\times66\ \mu m^2$. Fig. 5A and B shows the I(U) characteristics in dark and under IR radiation of the pm-Si:H and pm-Ge:H films, respectively. For the pm-Si:H sample, the increment of current from dark to IR radiation $\Delta I$ (at 10 V) is $0.8\times10^{-12}$ A, while for the pm-Ge:H sample, $\Delta I$ (at 10 V) is $1.8\times10^{-9}$ A.

From the above results, the current responsivity ($R_I$) was calculated and the corresponding voltage responsivity was extracted ($R_U$). The pm-Si:H film has a $R_I$ of $3.3\times10^{-7}$ A/W and a $R_U$ of $1.1\times10^6$ V/W, while the pm-Ge:H film has a $R_I$ of $7.3\times10^{-4}$ A/W and a $R_U$ of $5.2\times10^5$ V/W.

## 4. Discussion

The presence of nanocrystals in the cross section of the silicon and germanium films showed in Fig. 1, is an indication of the polymorphous nature of the films produced. That result was confirmed with the electrical measurements of the films, where $E_a$ and TCR were extracted, since these values are similar to those of a-Si:H and a-Ge:H [13,14].

The materials studied in this work are amorphous-like and the presence of nanocrystals does not affect significantly the properties

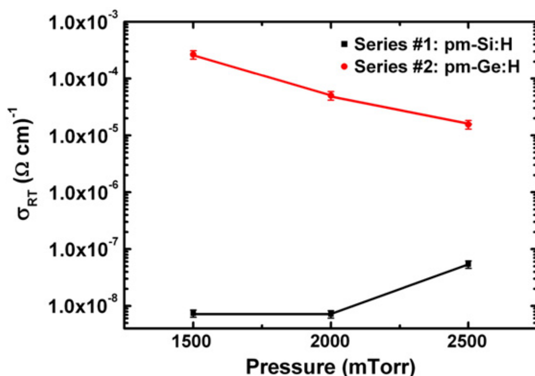


**Fig. 3.** Room temperature conductivity of polymorphous films as a function of the deposition pressure: series #1: pm-Si:H and series #2: pm-Ge:H.

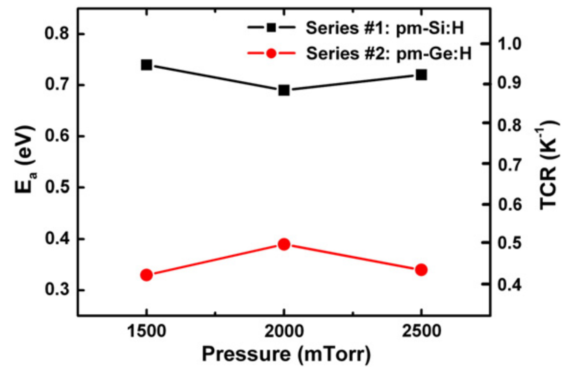


**Fig. 4.** Activation energy and TCR of polymorphous films as a function of the deposition pressure: series #1: pm-Si:H and series #2: pm-Ge:H.

of those materials (as $E_a$ or $E_g$), except for the transport properties as the electron mobility and stability [7–10].

In fact, the aim of studying polymorphous materials for thermal detection applications is to preserve the properties of intrinsic amorphous materials, as large $E_a$ and TCR (traduced in a large sensitivity to IR radiation), with an improvement in the film transport properties, as electron mobility and therefore conductivity. The nanocrystals do not improve the thermal detection in amorphous materials, but make them more stable, with better transport properties.

In Fig. 2 it is observed that the deposition rate ($V_d$) of the films has a strong dependence with the deposition pressure. Larger deposition pressures result in lower $V_d$ values. That trend can be related to the fact that at high deposition pressures (>1000 mTorr) the formation of nanocrystals in $SiH_4/H_2$ plasmas is stimulated [15], however very high pressures (~4000 mTorr) lead to the formation of powder in

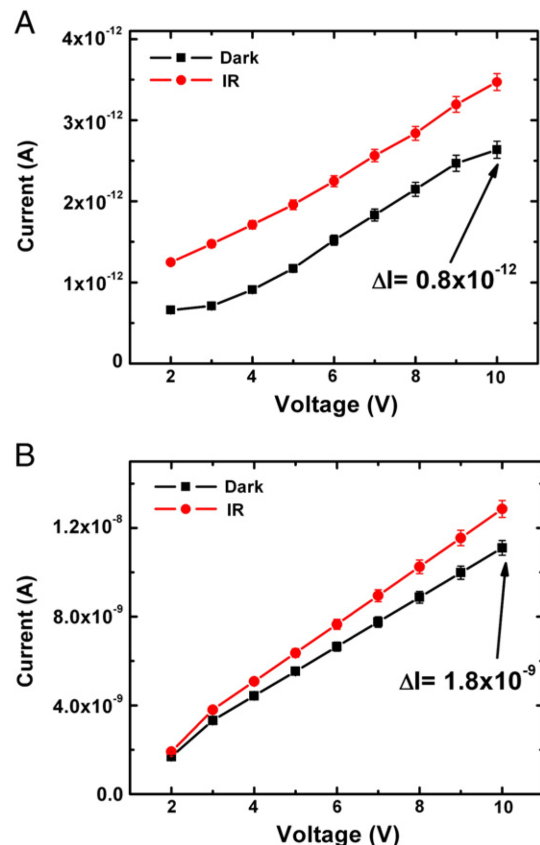


**Fig. 5.** I(U) characteristics in dark and under IR radiation of polymorphous films. A) series #1: pm-Si:H and B) series #2: pm-Ge:H.

**Table 1**
Performance characteristics of pm-Si:H and pm-Ge:H 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 | $GeH_4$ flow sccm | $H_2$ flow sccm | $R_I$ A/W | $R_U$ V/W | $E_a$ eV | TCR $K^{-1}$ | $\sigma_{RT}$ $(\Omega\ cm)^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| pm-Si:H film on glass | 2000 | 200 | 50 | No | 1000 | $3.3\times10^{-7}$ | $1.1\times10^{6}$ | 0.69 | 0.08 | $7\times10^{-9}$ |
| pm-Ge:H film on glass | 2000 | 200 | No | 50 | 1000 | $7.3\times10^{-4}$ | $5.2\times10^{5}$ | 0.39 | 0.05 | $2\times10^{-4}$ |
| a-Si:H film on glass [12] | 600 | 300 | – | No | No | – | – | 0.86 | 0.11 | $1\times10^{-9}$ |
| a-SiGe:H film on bridge [13] | 600 | 300 | 25 | 25 | 1000 | $2\times10^{-3}$ | $7.2\times10^{5}$ | 0.36 | 0.046 | $2\times10^{-5}$ |
| a-Si:H,B film on bridge [4] | – | <400 | – | No | – | – | $1\times10^{6}$ | 0.22 | 0.028 | $5\times10^{-3}$ |

the chamber, rather than a deposition of a film. The later is the possible reason of a decrement on $V_d$ when the films are deposited at high pressure.

From electrical characterization we observed a $\sigma_{RT}$ of pm-Ge:H of above four orders of magnitude larger than that of pm-Si:H. The $\sigma_{RT}$ of pm-Ge:H is close to that observed on a-Ge:H films deposited previously in the same LF-PECVD reactor [13], while the $\sigma_{RT}$ of pm-Si:H is larger in more than one order of magnitude than that measured on a-Si:H films deposited also in the same LF-PECVD reactor [13].

The largest conductivity measured in the pm-Ge:H films was of above $2\times10^{-4}(\Omega\ cm)^{-1}$, which is one order of magnitude shorter than that of a-Si:H,B, and one order of magnitude larger than that of the intrinsic a-SiGe:H film, which was studied in our previous work [13,14]. Even though the pm-Ge:H conductivity is one order of magnitude shorter than that of a-Si:H,B, its $E_a$ (0.39 eV) is almost twice than that of a-Si:H,B (0.22 eV). That result is very important, since $E_a$ is proportionally related to the TCR, using the expression: $TCR = -E_a/kT^2$.

The above discussion means that pm-Ge:H is much more sensitive to infrared radiation than a-Si:H,B despite a lower conductivity, which still is compatible with the CMOS readout circuit impedance.

In Fig. 3 is observed that the $\sigma_{RT}$ of pm-Si:H increases as the deposition pressure increases. This trend was also observed in our previous work [11], where pm-Si:H was deposited with different conditions. However, for pm-Ge:H just the opposite trend is observed. A straightforward explanation for the above behavior is quite complicated and several factors could be responsible. For instance, oxygen contamination on pm-Ge:H deposition could be the reason, since oxygen acts as impurity [16].

From current voltage measurement in dark and under IR radiation we observed in the pm-Si:H film a $\Delta I$ of $0.8\times10^{-12}$ A, which corresponds to a proportional increment in current of above 32%. For the pm-Ge:H film we observed a $\Delta I$ of $1.8\times10^{-9}$ A, which corresponds to a proportional increment in current of above 16%.

Despite that a proportional increment in current in pm-Si:H is two times larger than that of pm-Ge:H (resulted from a larger $E_a$ and TCR); the $\Delta I$ in pm-Ge:H is of above three orders of magnitude larger than that of pm-Si:H (resulted from its larger $\sigma_{RT}$).

The $E_a$, TCR, $R_I$ and $R_U$ values obtained in both series of films (series #1: pm-Si:H and series #2: pm-Ge:H) are shown in Table 1 and are compared with a-Si:H [13], a-SiGe:H [14] and boron doped a-Si:H (a-Si:H,B) [4], the latter is currently used in commercial microbolometer arrays. In Table 1 it is shown that the responsivity values of the polymorphous films deposited on glass are comparable or even larger than those reported for a-Si:H,B deposited on $SiN_x$ microbridges.

From our results we can conclude that pm-Si:H and pm-Ge:H have several advantages over a-Si:H and a-Si:H,B, respectively. Moreover, intrinsic pm-Ge:H seems to be a very promising material for high performance microbolometers due to its high Ea, TCR and an improved $\sigma_{RT}$.

## 5. Conclusions

In this work, we deposited polymorphous silicon (pm-Si:H) and polymorphous germanium (pm-Ge:H) by LF-PECVD and made a comparative study of their characteristics that are important for thermal detection, as $E_a$, TCR, $\sigma_{RT}$ and responsivity with IR radiation.

The influence of the deposition pressure on the film properties has been studied. Larger deposition pressures resulted in a significant decrement of the deposition rate in both types of films (pm-Si:H and pm-Ge:H). Also it was observed that the deposition pressure has an effect on the film conductivity. For the pm-Si:H films, the conductivity shows an increment as the deposition pressure increases, while, for the pm-Ge:H films, the tendency was the opposite.

Finally, from our results, we conclude that both, pm-Si:H and pm-Ge:H are promising materials to be used as thermo-sensing film in uncooled microbolometers, due to its advantages over a-Si:H and a-Si:H,B.

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