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Thermo-sensing silicon–germanium–boron films prepared by plasma for un-cooled micro-bolometers

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Abstract

In this work we report a study of silicon–germanium–boron alloys (a-$Si_xGe_yB_z$:H) deposited by low frequency plasma enhanced chemical vapor deposition (LF PECVD) at relatively low temperatures, which are compatible with the IC silicon technology for applications as low resistance thermo-sensing films in micro-bolometers. Three values of germanium gas content (Ge_y) were used during the film deposition, $Ge_y = 0.3$, 0.45 and 0.55. Deposition and film properties were compared with a reference intrinsic film (a-Si_xGe_y:H) in order to study the Ge_y effect on the temperature dependence of conductivity ($\sigma(T)$) and specifically on the activation energy (E_a). We observed a variation on the activation energy from $E_a = 0.34$ eV to $E_a = 0.18$ eV and on the room temperature conductivity from $\sigma_{RT} = 6 \times 10^{-5}\ (\Omega\,cm)^{-1}$ to $\sigma_{RT} = 2.5 \times 10^{-2}\ (\Omega\,cm)^{-1}$, for the reference intrinsic film and for the boron alloy with $Ge_y = 0.55$, respectively. The solid phase composition of the films was characterized by SIMS measurements. The effect of patterning the films (μm scale) with photolithography and the deposition on a SiN_x micro-bridge on the film electrical properties was also studied.

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Keywords: Amorphous semiconductors; Germanium; Silicon; Conductivity; Plasma deposition

1. Introduction

Amorphous silicon (a-Si:H) is a standard material used as thermo-sensing film in micro-bolometers and is fully compatible with the IC silicon technology [1–3]. This material has showed high activation energy (E_a) and consequently a high value of thermal coefficient of resistance (TCR) $\alpha = 0.39\ K^{-1}$, which is defined as $\alpha(T) = (1/R)|dR/dT| \approx E_a/kT^2$, where E_a is the activation energy, k is the Boltzmann constant and T is the temperature. However a-Si:H presents very high resistance, which results in a mismatch with the input impedance of the CMOS read-out circuits.

We have recently studied a-Si_xGe_y:H alloys as thermo-sensing films in micro-bolometers. These films showed high activation energy $E_a = 0.34$ eV and a high TCR value $\alpha = 0.043\ K^{-1}$, and improved, but still high cell resistance [4,5].

In this work, we present a study of silicon–germanium–boron alloys (a-$Si_xGe_yB_z$:H) deposited by low frequency PECVD at low temperature $T_s \approx 300$ °C and compatible with the silicon IC technology. We varied the germanium gas content Ge_y during the films deposition process in order to observe a reduction in its conductivity and the effect on the activation energy E_a. We compared these results with those of an intrinsic reference film (a-Si_xGe_y:H). Also it is discussed the effect on the electrical properties of the films studied, when they are patterned (μm scale) and deposited over a-SiN_x micro-bridge structure.

2. Experimental

The silicon–germanium–boron alloys (a-$Si_xGe_yB_z$:H) were deposited by low frequency (LF) PECVD in a

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capacitive discharge at frequency $f = 110$ kHz, substrate temperature $T_s = 300$ °C, pressure $P = 0.6$ Torr and RF power $W = 350$ W. Three sets of films were deposited from SiH_4, GeH_4, B_2H_6 and H_2 gas mixture, with a fixed SiH_4, B_2H_6 and H_2 gas flow rates: $Q_{SiH_4} = 50$ sccm, $Q_{B_2H_6} = 5$ sccm and $Q_{H_2} = 500$ sccm, respectively, while the GeH_4 gas flow was set at the following values: $Q_{GeH_4} = 25$, 50 and 75 sccm. This resulted in a Ge gas content $Y = 0.3$, 0.45, 0.55 and a B gas content $Z = 0.11$, 0.09, 0.07 in the samples labeled as process number 478, 479 and 480, respectively. An intrinsic film (a-Si_xGe_y:H) was deposited in order to compare its characteristics with that of the boron alloys, labeled as process number 443. This film was deposited under the same conditions as used for the boron alloys, with different gas mixture: SiH_4, GeH_4 and H_2; with gas flow rates: $Q_{SiH_4} = 25$ sccm, $Q_{GeH_4} = 25$ sccm and $Q_{H_2} = 1000$ sccm, respectively. This result in a Ge gas content $Y = 0.5$.

Since those films are researched for applications as low resistance thermo-sensing films for micro-bolometers, we studied the films electrical properties after patterning them with photolithography to one cell dimensions ($70 \times 66\ \mu m^2$). Assuming that stress arisen in the film deposited over a SiN_x micro-bridge could have an effect on the film conductivity, we also studied the films deposited on a micro-bridge. For that purpose, we prepared three different kinds of samples for each type of the four thermo-sensing films (three boron alloys with different Ge_y content and the intrinsic reference film).

The first kind of sample is commonly used for E_a and σ measurements and it is prepared as follows: a 0.2 μm titanium (Ti) stripes are deposited over a glass ('Corning 1737'), the stripes have a length of 10 mm and are separated by 1.5 mm distance and the thermo-sensing film is deposited over them. A photolithographic process is performed in order to etch part of the film leaving the Ti stripes uncovered, which will be the contacts for the electrical measurements. Fig. 1(a) shows that sample labeled as 'stripes sample'.

The second kind of sample is prepared in the following way: a Ti layer is deposited on a glass substrate and is patterned with photolithography in order to form stripes with length $L = 66$ μm separated by a distance $D = 40$ μm. Over the stripes is deposited the thermo-sensing film, which is also patterned. The dimensions of the thermo-sensing film are $70 \times 66\ \mu m^2$. Fig. 1(b) shows this sample labeled as 'patterned sample'. This sample allows us to observe dimensions and 'fabrication' effect on the conductivity.

The third sample consists of a SiN_x micro-bridge fabricated with surface micro-machining techniques and over it is deposited the thermo-sensing film, it is prepared as follows: a 2.5 μm-thick sacrificial aluminum (Al) layer is deposited by e-beam evaporation. A 0.8 μm-thick SiN_x film was deposited at low temperature $T_s = 350$ °C by low frequency PECVD over the Al sacrificial film. The SiN_x film is patterned by reactive ion etching (RIE) in order to form the micro-bridge and the Al sacrificial layer is etched. Ti contacts are deposited and patterned by photolithography over the SiN_x micro-bridge. Finally the thermo-sensing film is deposited and patterned over the Ti contacts. The dimensions of the film in this configuration are $70 \times 66\ \mu m^2$. Fig. 1(c) shows this kind of sample labeled as 'micro-bridge sample'. The different samples fabricated for characterization are listed in Table 1.

We performed measurements of temperature dependence of conductivity $\sigma(T)$ in the above samples, in the range of $T = 300$–400 K. The measurements were performed in a vacuum chamber at a pressure $P = 20$ mTorr. A temperature controller (model K-20, MMR Inc.) for the temperature measurement control and an electrometer (model 6517-A, Keithley Inst.) for the current measurements were employed. These measurements allowed us to obtain the $\sigma(T)$ temperature dependence and then to determine the E_a, the TCR and the room temperature conductivity, σ_{RT}.

The composition in solid phase of the different films was characterized by secondary ion mass spectroscopy (SIMS). The SIMS profiles were measured with a Cameca IMS-6f ion microprobe. Sputtering during SIMS utilized a cesium ion beam with primary ion energy from 5 to 15 keV. The solid solution composition was analyzed with a special

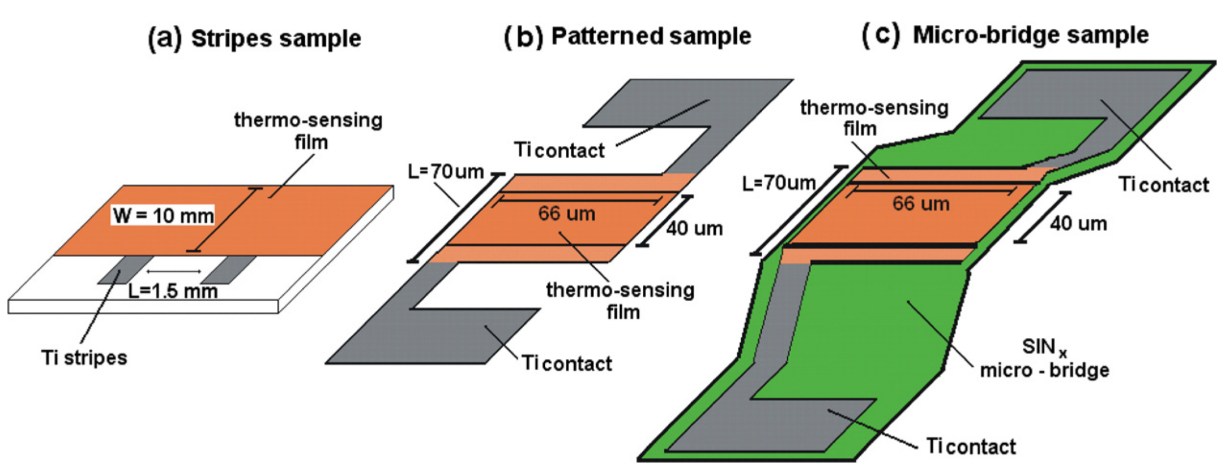

Fig. 1. Three different samples for electrical characterization: (a) stripes, (b) patterned and (c) micro-bridges.

Table 1
Gas and solid content in the different thermo-sensing films and the samples available for characterization

		Thermo-sensing films			
		Process 478	Process 479	Process 480	Process 443
Gas mixture		SiH_4: 50 sccm GeH_4: 25 sccm B_2H_6: 5 sccm	SiH_4: 50 sccm GeH_4: 50 sccm. B_2H_6: 5 sccm	SiH_4: 50 sccm GeH_4: 75 sccm B_2H_6: 5 sccm	SiH_4: 25 sccm GeH_4: 25 sccm H_2: 1000 sccm
Gas content	Si_x	0.59	0.46	0.38	0.5
	Ge_y	0.3	0.45	0.55	0.5
	B_z	0.11	0.09	0.07	0
Film thickness (μm)		0.36	0.42	0.51	0.5
Deposition rate (Å/s)		6	7	9.5	2.8
Solid content obtained from SIMS	Si_x	0.078	0.05	0.04	0.11
	Ge_y	0.59	0.67	0.71	0.88
	B_z	0.32	0.26	0.23	2.0×10^{-5}
Samples		#1: stripes #5: patterned Not available	#2: stripes #6: patterned #9: micro-bridge	#3: stripes #7: patterned #10: micro-bridge	#4: stripes #8: patterned #11: micro-bridge

mode in which secondary ions CsM^+ (where M is the analyzed element) were monitored during cesium sputtering. Oxygen flooding was always used with this mode in order to minimize the SIMS matrix effect found in SiGe compounds.

3. Results

The conductivity temperature dependence can be well described by $\sigma(T) = \sigma_0 \exp(-E_a/kT)$, where σ_0 is the prefactor, E_a is the activation energy, k is the Boltzmann constant and T is the temperature. Fig. 2 shows $\sigma(T)$ curves for four different thermo-sensing films (three boron alloys with different Ge_y gas content, $Ge_y = 0.3$, 0.45, 0.55 and the intrinsic film with $Ge_y = 0.5$), fabricated in three different sample configurations (stripes, patterns and micro-bridges).

We observed that an increment in the Ge_y content in gas phase in the boron alloys results in an increase of the room temperature conductivity, from $\sigma_{RT} = 2.8 \times 10^{-3}\ (\Omega\ cm)^{-1}$ (for $Ge_y = 0.3$) to $\sigma_{RT} = 1 \times 10^{-2}\ (\Omega\ cm)^{-1}$ (for $Ge_y = 0.45$) and $\sigma_{RT} = 2.5 \times 10^{-2}\ (\Omega\ cm)^{-1}$ (for $Ge_y = 0.55$), while for the intrinsic film the room temperature conductivity

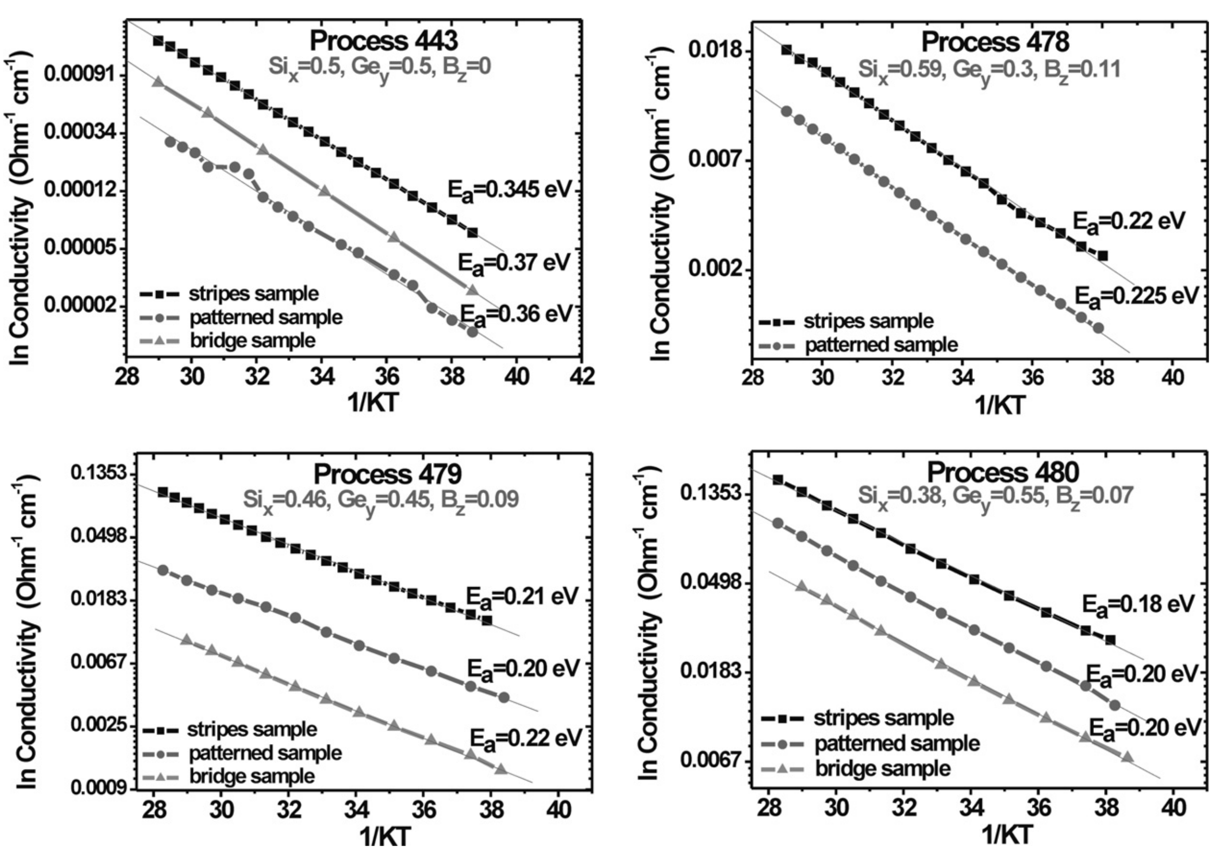

Fig. 2. Conductivity dependence with temperature for the different thermo-sensing films (process: 443, 478, 479 and 480).

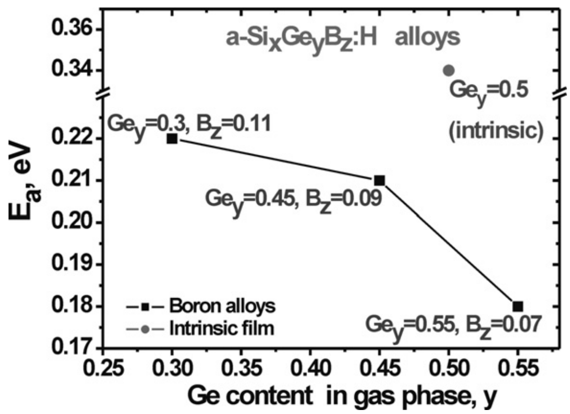

Fig. 3. E_a as function of Ge gas content, Ge_y, in the boron alloys, a-$Si_xGe_yB_z$:H.

is $\sigma_{RT} = 6 \times 10^{-5}$ $(\Omega\,cm)^{-1}$ (for $Ge_y = 0.5$). We observed a reduction in E_a in the boron alloys, $E_a = 0.22$ eV (for $Ge_y = 0.3$), $E_a = 0.21$ eV (for $Ge_y = 0.45$) and $E_a = 0.18$ eV (for $Ge_y = 0.55$), while in the intrinsic film is $E_a = 0.345$ eV (for $Ge_y = 0.5$). The E_a as a function of Ge_y is shown in Fig. 3.

From SIMS we obtained the solid composition in the thermo-sensing films. For the film with gas content: $Ge_y = 0.3$ and $B_z = 0.11$ (process 478), we observed an increase in the solid content: $Ge_y = 0.59$ and $B_z = 0.32$, respectively. For the film with $Ge_y = 0.45$ and $B_z = 0.09$ (process 479), we observed $Ge_y = 0.67$ and $B_z = 0.26$, respectively and for the film with $Ge_y = 0.55$ and $B_z = 0.07$ (process 480), we observed $Ge_y = 0.71$ and $B_z = 0.23$, respectively.

4. Discussion

From $\sigma(T)$ measurements with temperature in the thermo-sensing films, we found that the boron alloys (a-$Si_xGe_yB_z$:H) have a significantly larger conductivity (by about 2–3 orders of magnitude) in comparison with that of the intrinsic reference film (a-Si_xGe_y:H). The increment in σ in the a-$Si_xGe_yB_z$:H films is accompanied with a reduction in E_a, in the range of 36–47%, depending on the Ge_y content.

The reduction in the thermo-sensing films dimensions, from the stripes samples (10×1.5 mm^2) to the patterned samples (70×66 μm^2), has no significant effect on the E_a, however it has on the σ. We observed a reduction by 50–80% of the σ value in the patterned samples in comparison with that of the stripes samples.

A slight increase in the E_a of the thermo-sensing films deposited over a SiN_x micro-bridge was observed, in comparison with that of the stripes and patterned samples, however the micro-bolometer samples showed a larger reduction in the σ values, around 60–90%. Table 2 shows the values of E_a, TCR, σ_{RT} and σ_0 of the different samples. The Ge_y content and the sample structure dependence of σ are shown in Fig. 4.

SIMS results suggested a strong preferential B and Ge incorporation from gas phase during the film deposition process. The B_z solid content demonstrated values about 3 times larger than the content in gas phase B_z, while the Ge_y solid content increased by a factor of 1.3–2 from the Ge_y gas content. Those results are shown in Table 1.

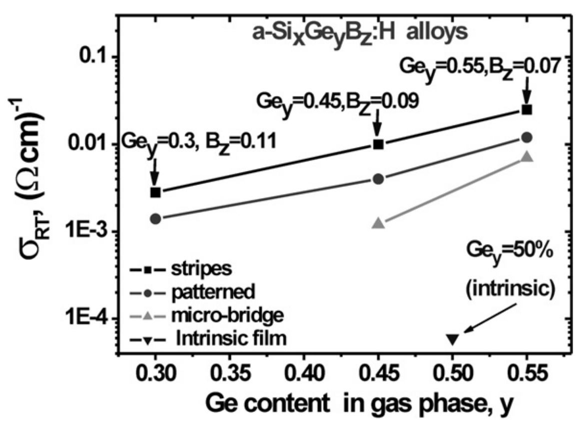

Fig. 4. Conductivity dependence on the Ge gas content, Ge_y.

Table 2
Comparison of E_a, TCR, σ_{RT} and σ_0 in stripes, patterned and micro-bridges samples for the different thermo-sensing films

		Thermo-sensing films			
		Process 478	Process 479	Process 480	Process 443
Stripes samples	E_a (eV)	0.22	0.21	0.18	0.345
	TCR (K^{-1})	−0.028	−0.027	−0.023	−0.044
	σ_{RT} $(\Omega\,cm)^{-1}$	2.8×10^{-3}	1×10^{-2}	2.5×10^{-2}	6×10^{-5}
	σ_0 $(\Omega\,cm)^{-1}$	12.02	36.46	24.55	34.85
Patterned samples	E_a (eV)	0.225	0.20	0.20	0.36
	TCR (K^{-1})	−0.029	−0.025	−0.025	−0.046
	σ_{RT} $(\Omega cm)^{-1}$	1.4×10^{-3}	4×10^{-3}	1.2×10^{-2}	1.08×10^{-5}
	σ_0 $(\Omega cm)^{-1}$	7.27	8.23	28.26	11.13
Micro-bridge samples	E_a (eV)	Not available	0.22	0.20	0.37
	TCR (K^{-1})		−0.028	−0.025	−0.047
	σ_{RT} $(\Omega cm)^{-1}$		1.2×10^{-3}	7×10^{-3}	2.2×10^{-5}
	σ_0 $(\Omega cm)^{-1}$		5.94	15.58	32.8

5. Conclusions

From the conductivity characterization in the thermo-sensing films, we can state that the boron alloys (a-Si_x-Ge_yB_z:H) demonstrated an increment in their conductivity (between 2 and 3 orders of magnitude) in comparison of that of the intrinsic film (a-Si_xGe_y:H). The values of σ_{RT} in the boron alloys are $\sigma_{RT} = 2.8 \times 10^{-3}$, 1×10^{-2} and 2.5×10^{-2} $(\Omega\,cm)^{-1}$ for $Ge_y = 0.3$, 0.45 and 0.55, respectively; while for the intrinsic film is $\sigma_{RT} = 6 \times 10^{-5}$ $(\Omega\,cm)^{-1}$ for $Ge_y = 0.5$. The increment in σ was accompanied by a reduction in E_a, from $E_a = 0.345$ eV for the intrinsic film to $E_a = 0.22$, 0.21 and 0.18 eV for $Ge_y = 0.3$, 0.45 and 0.55, respectively, in the boron alloys. The reduction in the thermo-sensing films dimensions has no significant effect on the E_a, however a reduction of 50–80% in the σ was observed. In the micro-bridge samples we found a slight increment in E_a in comparison with the pattern and stripes samples, however these samples showed a larger reduction on σ (60–90%). From SIMS we obtained the solid composition in the thermo-sensing films. We observed a significant increase in the B and Ge solid content from the gas content, suggesting strong preferential B and Ge incorporation from gas phase.

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