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Piezoresistive properties of nanocrystalline silicon thin films deposited on plastic substrates by hot-wire chemical vapor deposition

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Abstract

The piezoresistive property of n-type and p-type nanocrystalline silicon thin films deposited on plastic (PEN) at a substrate temperature of 150 °C by hot-wire chemical vapor deposition, is studied. The crystalline fraction decreased from 80% to 65% in p-type and from 84% to 62% in n-type films, as the dopant gas-to-silane flow rate ratio was increased from 0.18% to 3-3.5%. N-type films have negative gauge factor (-11 to -16) and p-type films have positive gauge factor (9 to 25). In n-type films the higher gauge factors (in absolute value) were obtained by increasing the doping level whereas in p-type films higher gauge factors were obtained by increasing the crystalline fraction. © 2006 Elsevier B.V. All rights reserved.

Keywords: Nanocrystalline silicon; Piezoresistivity; Hot-wire chemical vapor deposition; Flexible electronics

1. Introduction

The piezoresistive property of crystalline silicon has long been known to scientists and engineers [1–4] and most straingauge sensors use that property as their operation principle [3–5]. These devices measure strain from the relative resistance change of a Si transducer that is deformed to the strain to be measured. Piezoresistance in c-Si is highly anisotropic and is described by a set of coefficients that are the elements of the rank-4 piezoresistive tensor, relating the change in electrical resistivity in a particular crystallographic direction to the components of the applied stress tensor. Due to the symmetry of the silicon fcc crystal structure the piezoresistive tensor has only three independent elements, namely π_{11} , π_{12} and π_{44} [1] where the indexes have the usual meaning in six-component vector notation.

Polycrystalline metallic strain-gauge sensors are also common but they are much less sensitive than their semiconductor counterparts [5]. This is because their operation is mainly based on resistance variation due to stress-induced dimensional changes and not on large changes on the resistivity, as is the case with Si (or Ge) sensors. Volume changes due to strain affect

both carrier concentration and carrier mobility in a semiconductor and in this way they lead to resistance changes. But more important, deformation potentials modify the band structure near the edge of the conduction and valence bands leading to changes in carrier effective mass and/or occupancy of the density of states at energies close to the Fermi level. This mechanisms dramatically enhance the piezoresistive effect in Si (also in Ge, C-diamond and other semiconductors) when compared to metals [1,5]. As the Fermi level position approaches the conduction or valence band edges the effect is expected to be enhanced and therefore piezoresistance is more important in doped than in intrinsic Si. However, both the physical origin and the corresponding values of the piezoresistive coefficients are very different in p- and n-type material. Detailed studies of both mechanisms can be found in the literature [1-4].

The piezoresistive effect has also been found in thin crystalline silicon films [6,7]. Due to the semi-crystalline nature of these films the reported effect is rather isotropic and it broadly averages the resistance changes of the randomly oriented crystallites, thus retaining the signal of the largest c-Si piezoresistive coefficient. Moreover, grain boundaries also play a role in piezoresistance of nanocrystalline films and their net effect is to attenuate resistivity changes occurring in the crystalline grains [8,9].

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In this paper, the piezoresistive effect in flexible n- and p-type hydrogenated nanocrystalline silicon thin films, nc-Si:H, deposited on inexpensive plastic substrates by the hot-wire chemical vapor deposition technique (HWCVD) will be studied as a function of crystalline fraction, gas-phase dopant concentration and position of the Fermi level. The parameter used to describe the piezoresistive effect in the present work is the gauge factor, GF, defined as the relative resistance change per unit axial strain: $\Delta R / R = GF \times \varepsilon$, where *R* is electrical resistance and ε is axial strain. In this expression the factor $(1 + 2\nu)\varepsilon$ where ν is the Poisson ratio, which accounts for the resistance change due to geometrical changes of the sample caused by strain, was removed from the second member of the equation since it is very small when compared to the piezoresistive effect.

2. Experimental details

2.1. Film preparation

All the films were deposited in an ultra-high vacuum HWCVD chamber equipped with load lock. The pumping system, consisting of a molecular drag pump and a rotary vane pump, allowed to achieve a base pressure lower than 10^{-7} Torr. The substrate holder was placed 5 cm above a single tantalum filament (\emptyset =0.5 mm, 14 cm long) that was bent to a coil. The filament was resistively heated ($T_{\rm fil} \sim 1770$ °C) for deposition, using a DC power supply ($I_{\rm fil}$ =13.5 A) that pyrolitically decomposed the reactant gases at the filament surface.

nc-Si:H films were deposited using 95% hydrogen dilution $(D_{\rm H})$ of reactant gases, defined as the H₂ flow rate divided by total gas flow rate × 100%. n- and p- type gas-phase doping was achieved by adding 98% H₂-diluted phosphine or diborane, respectively, to the silane–hydrogen gas mixture (see Table 1). Two series of samples were deposited by varying the dopant gas-to-silane flow rate ratio, $F=F_{\rm dopant}/F_{\rm SiH4}$. Since P- and B-doping was performed in the same HWCVD chamber a 2 µm thick sacrificial layer of intrinsic a-Si:H was deposited between the doping series in order to avoid cross contamination.

Table 1			
Properties of n- an	d p-type samp	les prepared b	v HW-CVD

	1 2		1 2			
Sample	PH ₃ , B ₂ H ₆ / SiH ₄ ×100%	Thickness <i>t</i> _f (nm)	$\sigma_{ m d} \ (\Omega^{-1} \ m cm^{-1})$	$E_{\rm a}, \sigma$ (meV)	$X_{\rm C}$	GF
N192	0.15	169	0.57	61	0.78	-10.8
N185	1.0	190	0.30	82	0.80	†
N183	1.5	174	1.07	49	0.77	-12.9
N186	2.0	187	3.50	36	0.75	-19.0
N222	2.5	148	1.35	28	t	-14.3
N191	3.0	183	2.39	39	0.65	-16.0
P214	0.18	163	2.72×10^{-5}	580	0.84	t
P216	1.0	182	0.34	101	0.81	25.3
P217	1.5	186	1.46	72	0.78	24.5
P220	2.0	170	1.96	61	0.74	15.1
P218	2.5	185	3.27	40	0.72	10.3
P219	3.0	178	1.44	32	0.69	13.3
P221	3.5	174	2.33	45	0.62	9.1

(†) Not measured.

75 µm-thick polyethylene naphthalate (PEN) (maximum working temperature is 155 °C) was used as substrate. Substrate temperature (T_{sub}) during deposition, measured by a thermocouple embedded in the back side of the substrate holder, was 150 °C. During deposition time (~ 10 min) no increase in T_{sub} was detected. Glass substrates were placed side by side with the PEN substrates during all depositions for comparison and to allow for Raman measurements (see next section).

2.2. Film characterization

Raman spectroscopy was used to obtain crystalline fraction of the films. In this case films were deposited on glass substrates, since Raman spectrum of PEN substrates contains a sharp pick at 520 cm^{-1} which exactly overlaps the TO phonon mode of crystalline Si. The Raman spectra were obtained with a Jobin-Yvon T64000 spectrometer using a 514 nm Ar-laser line. The crystallinity was determined from the amplitudes of crystalline and amorphous bands using the formula $X_{\rm C} = I_{\rm c}$ / $(I_{c} + \gamma I_{a})$, where I_{c} and I_{a} are the amplitudes of crystalline and amorphous Raman peaks, respectively, and y=1.25 is an empirical coefficient expressing the ratio of Raman crosssections for both bands [10]. Film thickness was calculated from the interference fringes in the optical transmission spectra obtained with a Shimadzu UV-3101PC spectrophotometer. Dark conductivity, σ_d , measurements were performed in the temperature range from 20 °C to 95 °C, during the cooling part of the cycle, between Al evaporated parallel contacts 6 mm wide, 1 mm apart. The activation energy of σ_d , E_a , was calculated from the slope of an Arrhenius plot of σ_d as a function of 1000 / T (T is temperature in K). Room-temperature (RT) dark conductivity was extrapolated from the linear region of the curve that was fit to the data in the Arrhenius plot. The relative content of P in the films was evaluated by TOF-SIMS.

The piezoresistive property was studied by quasi-static mechanical tests performed in a *Polymer Laboratories* MINI-MAT machine in the tensile mode at test velocity of dl / dt=0.02 mm min⁻¹ on ~ 35 mm × 10 mm rectangular samples, 0.075 mm thick. The variation of the electrical resistance of the samples with the applied axial strain was calculated from the slope of *I*–*V* curves measured in real time with an automated *Keithley* 487 picoammeter/voltage source and corresponding to several points of the force-deformation curves (see Fig. 1). *I*–*V* data points were collected between the same Al parallel contacts used for σ_d measurements. *I*–*V* curves were measured with the electric field applied and the current flowing parallel to the strain axis with applied voltage ranging between -3 V and + 3 V.

3. Results and discussion

Fig. 2 shows the crystalline fraction of p- and n-type films as a function of dopant gas-to-silane flow rate ratio. It can be seen that, in general, as the flow rate of the dopant gas was increased, the crystalline fraction of the doped film decreased, independently of the dopant gas added. X_C decreased from 80% to 65% when the phosphine-to-silane flow rate ratio increased from 1%

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