# Correlation of structural inhomogeneities with transport properties in amorphous silicon germanium alloy thin films

Ayana Bhaduri [a], Partha Chaudhuri [a,*], Stephane Vignoli [b], Christophe Longeaud [c]

[a] *Energy Research Unit, Indian Association for the Cultivation of Science, Kolkata-700032, India*
[b] *Laboratoire de Physique de la Matière Condensée et Nanostructures, Universite Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France*
[c] *Laboratoire de Génie Electrique de Paris, 91190 Gif sur Yvette, France*

## ABSTRACT

Amorphous silicon–germanium (a-$Si_{1-x}Ge_x$:H) alloy thin films were studied over a wide range of Ge content ($x=0$–1.00) grown by radio frequency plasma CVD (rf PECVD) technique with variation of different deposition parameters such as $H_2$ dilution, rf power and square wave pulse modulation (SWPM) of rf amplitude. Structural properties like microstructure factor ($R^*$) and AFM surface roughness ($R_{RMS}$) were correlated with the transport properties such as mobility-lifetime product ($\mu\tau$) and ambipolar diffusion length ($L_d$) of these films. Near the middle composition range ($x=0.32$–0.70), the $R^*$ in these films varies between 0.20 and 0.42 and $L_d$ ranges between 50 and 60 nm. Films deposited near the pure silicon and pure germanium ends have improved structural and transport properties. By SWPM method we have been able to significantly lower the $R^*$ value of the a-$Si_{1-x}Ge_x$:H films to 0.15 with $x=0.40$–0.45 resulting in $L_d=100$ nm and $\mu\tau=1.0\times10^{-6}$ cm$^2$ V$^{-1}$.

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## 1. Introduction

By controlling the Si/Ge ratio in hydrogenated amorphous silicon–germanium (a-$Si_{1-x}Ge_x$: H) alloy films, the band gap may be varied continuously from 1.75 eV (a-Si:H) to below 1 eV (a-Ge:H). In high efficiency amorphous silicon-based tandem solar cells, amorphous silicon–germanium (a-$Si_{1-x}Ge_x$:H) alloy material is used in the lower intrinsic layers in order to absorb the longer wavelength region of the visible solar spectrum [1]. However, with increasing Ge content chemical inhomogeneity increases that enhances the structural defects such as dangling bonds (DB), vacancies and microvoids and increase film hetero-geneity which in turn degrade the optoelectronic properties of the material [2]. For solar cells application it is necessary to reduce the microstructural inhomogeneity in amorphous silicon–germanium alloy (a-$Si_{1-x}Ge_x$:H) thin films deposited by 13.56 MHz rf plasma enhanced chemical vapour deposition (rf PECVD) method, which is so far the common industrial production technique for a-Si-related solar modules. In this paper we have studied the influence of various deposition parameters on the structural and electrical transport properties of the a-$Si_{1-x}Ge_x$:H films with an emphasis on rather high content of germanium ($x=0.4$–0.45). In particular, application of square wave pulse modulation (SWPM) of the rf amplitude has been

found to be a promising technique to control the nanostructures within the film with consequent improvement of the optoelec-tronic properties. SWPM method has been applied to deposit a-Si:H materials [3,4]. However, to our knowledge, our group were the first to carry out extensive studies on a-$Si_{1-x}Ge_x$:H films deposited by SWPM method [5–7].

## 2. Experimental

The a-$Si_{1-x}Ge_x$:H alloy thin films were deposited by 13.56 MHz rf PECVD from a mixture of $SiH_4$ and $GeH_4$ with total flow of 3.6 sccm (standard cubic centimeters per minute) and diluted in $H_2$ (96 sccm). Percentage of $GeH_4$ in the $SiH_4$ and $GeH_4$ mixture was varied from 0% to 100%. For the middle composition range ($x=0.40$–0.50) we varied the rf power density from 40 to 197 mW/cm$^2$ to study the effect of rf power density on microstructure and optoelectronic properties of the layers. Starting with the samples deposited in the intermediate range of Ge concentration ($x=0.40$–0.45) and at the rf power density for which the microstructure is rather low we applied square wave pulse modulation (SWPM) of the rf amplitude in order to regulate the fine particle incorporation to the a-$Si_{1-x}Ge_x$:H alloy films and thereby to further reduce the microstructures. Details of the SWPM method have been described elsewhere [6]. The structural properties of the a-$Si_{1-x}Ge_x$:H films were studied by Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM). Ge content was determined from micro-Raman spectroscopy [6]. Mobility-lifetime product

$(\mu\tau)$ was derived from photoconductivity with a flux of $10^{14}$ cm$^{-2}$ s$^{-1}$ of 740 nm monochromatic light. Photosensitivity ($S$) was calculated from the ratio of photoconductivity ($\sigma_{Ph}$) to dark conductivity ($\sigma_D$) where $\sigma_{Ph}$ was measured under white light (AM 1.5 using a class 1 solar simulator) of 100 mW/cm$^2$ intensity. The ambipolar diffusion length ($L_d$) was measured by steady state photocarrier grating method (SSPG).

## 3. Results

### 3.1. Properties of the a-Si$_{1-x}$Ge$_x$:H films deposited with change in Ge content at constant rf power

Films of a-Si$_{1-x}$Ge$_x$:H with various $x$ values were deposited with a rf power density of 110 mW/cm$^2$ and we have measured the evolution of $L_d$ with the Ge content ($x$) of the films. Microstructure factor ($R^*$) and AFM surface roughness ($R_{RMS}$) were used to measure the structural inhomogeneity of the films for the entire range of Ge content from $x=0$–1.00, $R^*$ is defined as [8]

$$R^* = \frac{[SiH_2]_n}{[SiH]+[SiH_2]_n} + \frac{[GeH_2]_n}{[GeH]+[GeH_2]_n} \qquad (1)$$

The evolution of $L_d$, $R^*$ and the bonded H content $C_H$ with Ge content is shown in Fig. 1. We note that there is a striking correspondence between $R^*$ and $L_d$, i.e. $L_d$ is high where $R^*$ is low and vice versa. For pure a-Si:H ($x=0$) the $R^*$ equals 0.1 and increases to 0.42 for $x=0.32$. In the composition range $x=0.32$–0.70 of Ge, $R^*$ varies between 0.42 and 0.2, but, $R^*$ becomes quite low (0.07) for the pure a-Ge:H sample. $L_d$ is maximum (150 nm) for a-Si:H and varies between 45 and 55 nm in the range $x=0.32$–0.70 and increased to 65 nm for a-Ge:H. The bonded H content ($C_H$) in these samples follows the $R^*$ evolution and also decreases with increasing Ge content (Fig. 1).

The RMS surface roughness of the a-Si$_{1-x}$Ge$_x$:H films deposited with various Ge content is shown in Fig. 2. The surface roughness ($R_{RMS}$) increases from 1 nm for a-Si:H to a maximum of 2.8 nm for a-Si$_{1-x}$Ge$_x$:H with Ge content $x=0.70$ and then again decreases to a value of 1.2 nm for a-Ge:H.

### 3.2. Properties of the samples deposited with variation of rf power density

From Fig. 3 we observe that with the increase in rf power density from 40 to 197 mW/cm$^2$, the microstructure factor $R^*$ gradually decreases from 0.31 to 0.22. The effect of structural



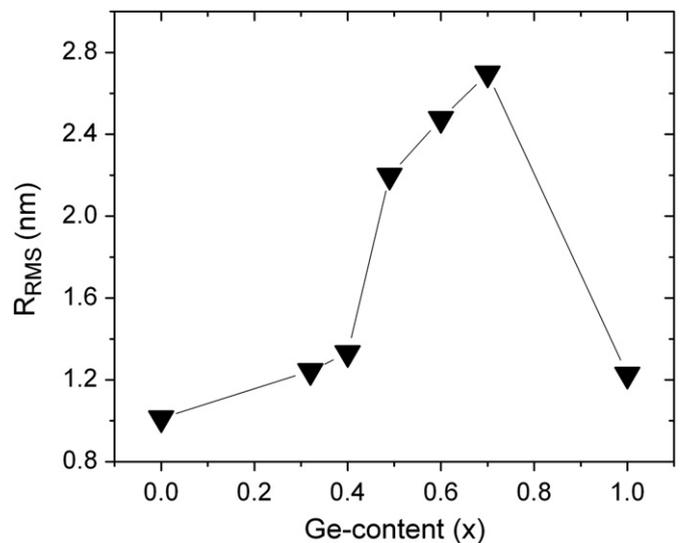**Fig. 2.** The RMS surface roughness ($R_{RMS}$) of the a-Si$_{1-x}$Ge$_x$:H films deposited with various Ge content ($x$).
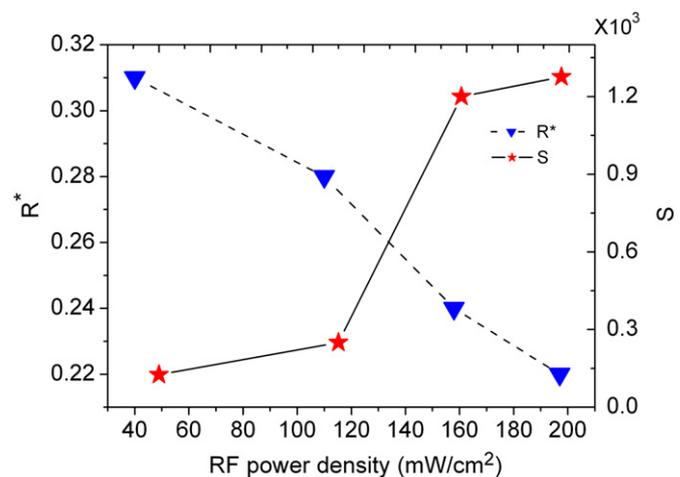


**Fig. 3.** Evolution of the IR microstructure factor $R^*$ and the photosensitivity $S$ with RF power density variation.

improvement with increase in power density is also reflected in the photosensitivity ($S$) which increases by an order of magnitude over the power density range (Fig. 3).
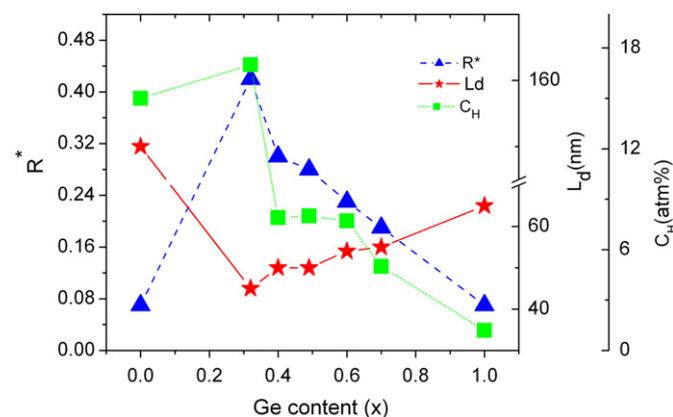
### 3.3. Properties of the samples deposited by SWPM

Maintaining the Ge content in the a-Si$_{1-x}$Ge$_x$:H in intermediate range ($x=0.40$–0.45) and with rf power density of 197 mW/cm$^2$ we next applied square wave pulse modulation (SWPM) of the rf amplitude. Variable parameter chosen for the SWPM is the duty cycle ($DC$) defined as, $DC=[T_{on}/(T_{on}+T_{off})] \times 100\%$, where $T_{on}$ and $T_{off}$ are the plasma "on time" and "off time" respectively, the total pulse cycle period ($T_{on}+T_{off}$) being kept constant at 737 μs. The variations of $S$ and $R^*$ of the films deposited at different $DC$ are shown in Fig. 4. Photosensitivity sharply increases as we go from the continuous mode ($DC=100\%$) to the SWPM mode. The film deposited at $DC=75\%$ has the highest photosensitivity of 2870. This value is quite high for the a-SiGe:H alloy films having band gap of 1.45 eV. $R^*$ decreases from 0.22 in continuous mode to about 0.15 at $DC=75\%$ and slightly increases to 0.18 when $DC$ is lowered to 50%.
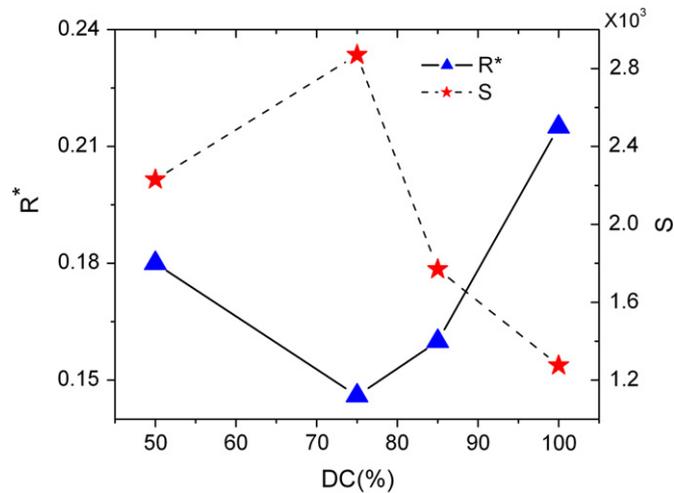


**Fig. 1.** Evolution of ambipolar diffusion length $L_d$, IR microstructure factor $R^*$ and hydrogen content $C_H$ with Ge content ($x$).

**Fig. 4.** Evolution of the IR microstructure factor $R^*$ and the photosensitivity $S$ with duty cycle ($DC$).
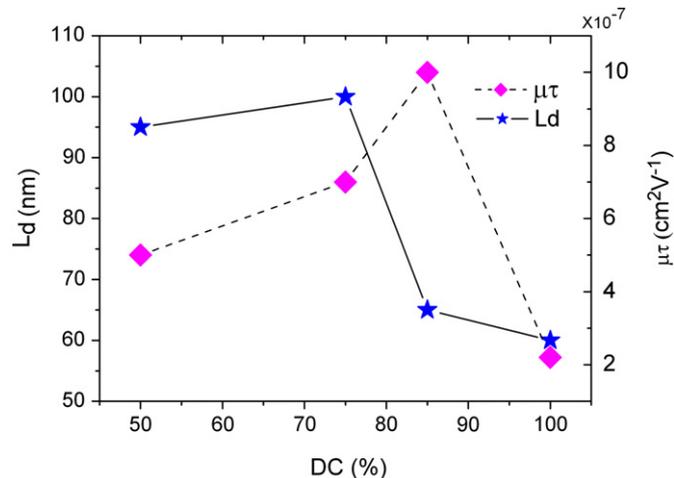


**Fig. 5.** Evolution of the ambipolar diffusion length $L_d$ and the mobility-lifetime product ($\mu\tau$) with the duty cycle ($DC$).



**Fig. 6.** The RMS surface roughness ($R_{RMS}$) of the a-Si$_{1-x}$Ge$_x$:H films deposited at various duty cycles ($DC$).

We have plotted the evolution of the ambipolar diffusion length $Ld$ and mobility-lifetime product ($\mu\tau$) with the duty cycle in Fig. 5. $Ld$ becomes maximum (100 nm) for $DC$ of 75%. $\mu\tau$ reaches its maximum ($1 \times 10^{-6}$ cm$^2$ V$^{-1}$) at the $DC$ of 85%.

The RMS surface roughness ($R_{RMS}$) of the a-Si$_{1-x}$Ge$_x$:H films deposited with various duty cycle are shown in Fig. 6. Statistical analysis of the surface roughness shows that there is a significant increase in $R_{RMS}$ from 1 to 12 nm with the lowering of the $DC$ from 100% to 50%.

## 4. Discussion

From Fig. 1 we see that structural inhomogeneity (characterized by $R^*$) is high in a-Si$_{1-x}$Ge$_x$:H alloy films over the middle composition range of $x=0.32$–0.7. It has been observed that in a-SiGe the compositional disorder and long range potential fluctuations are largest over the middle composition range [9,10]. The structural and transport properties of the films have been found to improve [11] towards Si or Ge end like in crystalline SiGe [12]. The various microstructural inhomogeneities in a-Si$_{1-x}$Ge$_x$:H alloy films may be grouped under two types namely (1) intrinsic and (2) extrinsic types [13]. The inhomogeneity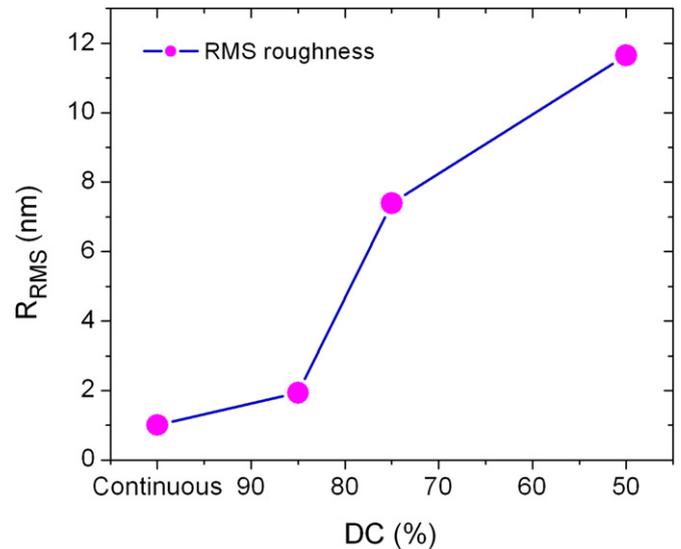 related to non-uniform distribution of Ge atoms and Ge cluster formation with increasing Ge content and the preferential attachment of the hydrogen to the Si-related dangling bonds in the amorphous matrix may be regarded as the intrinsic-type inhomogeneity. The extrinsic type of inhomogeneities result from the incorporation of particles from the plasma, microvoids, hydrogen clusters on the surface of the voids and the nanostructures. Deposition of device quality a-Si$_{1-x}$Ge$_x$:H films demands the control of all these sources of inhomogeneities.

In the Ge content variation series at constant rf power, we have observed that increase in Ge content results in increased chemical inhomogeneity that enhances the structural defects. However, we observe that while $R^*$ becomes maximum at $x=0.32$, the surface roughness $R_{RMS}$ maximizes at $x=0.70$. This apparent difference in the nature of variation of these two structural parameters may be explained as follows. $R^*$ is estimated from the amounts of hydrogen bonded in monohydride mode and polyhydride mode to Si and Ge sites (Eq. (1)). Polyhydride-type bonding is an indicator of disorder of the material. With addition of Ge within the Si matrix there is an increase in the compositional inhomogeneity, which is reflected in the high value of $R^*$. However, above $x=0.50$ the inhomogeneity gradually decreases as also $R^*$. Moreover, since hydrogen is preferentially bonded with Si there is a decreasing tendency in $C_H$ with increase in Ge content (Fig. 1) [14]. On the other hand $R_{RMS}$ may be correlated with Ge clustering which increases with the increase in Ge content within Si matrix [15]. Actually, with increase in the GeH$_4$ content in the gas mixture, growth mechanism changes from homogeneous to inhomogeneous nature. Ge-related radicals having high reactivity on the growing surface [16] are less mobile than the Si-related radicals. Due to higher surface mobility the incident Si-related radicals can diffuse longer on the growing surface than Ge-related ones. The absorbed Ge-related radicals are thus accumulated on the growing surface to form the Ge clusters. These will induce the inhomogeneous growth process (island growth mode) and the top surface roughness ($R_{RMS}$) gradually increased with $x$. At a-Ge:H end ($x=1.00$), however, the Ge clustering disappears resulting in a low $R_{RMS}$ value.

With increasing rf power (Fig. 3) there is an increase of the bombardment of the growth surface by ions and high energy gas precursors, which lead to an increase in the surface diffusion length of incident radicals. So films with homogeneous

microstructure are produced [17]. Decrease of $R^*$ value with increasing rf power density may thus be explained. However, too much increase of rf power density causes "peeling off" of the layer. Hence we restricted the power density to 197 mW/cm$^2$.

The technique of SWPM of rf amplitude of conventional 13.56 MHz rf PECVD applied to the deposition of a-Si$_{1-x}$Ge$_x$:H improves the film microstructure $R^*$ as seen from the Fig. 4. Since the size of the clusters formed within the plasma depends on their residence time within the plasma, pulsing the plasma "on" and "off" at regular intervals should interrupt the cluster formation process. Besides, the clusters are swept away by the gas flow during the "off" time. Thus with decrease in DC the size of the nanostructures incorporated from the plasma decreases. However, decrease of DC also means the decrease in the bombardment by the ions of the growth surface. This will result in a reduced mobility of the precursors with concomitant increase in surface roughness (Fig. 6). The combined effect of reduced size of the incorporated particles and reduction in ion bombardment gives rise to a minimum in the value of $R^*$ at DC=75%. From transmission electron microscopic study we have also observed some of the nanostructures are actually nanocrystallites of SiGe. An enhancement of the Ge content in the SiGe nanocrystallites has been observed with the reduction in nanocrystal size (to be published elsewhere). The overall effect of these nanostructural changes on the transport properties of the material is however, beneficial, as reflected in the improvement of $S$ (Fig. 4), $L_d$ and $\mu\tau$ (Fig. 5). Thus, by controlling the cluster formation in the plasma by SWPM we could reduce the extrinsic type of inhomogeneities resulting in improved optoelectronic properties for the a-Si$_{1-x}$Ge$_x$:H samples.

## 5. Conclusion

Effects of compositional disorder on the properties of a-Si$_{1-x}$Ge$_x$:H alloy films have been studied. In the middle composition range of $x$=0.32–0.70 the structure of the films is poor due to the presence of large clusters of Ge. Increase of the rf power reduces microstructures but for device applications we need to reduce the microstructures further. Powders formed in the plasma contribute largely to the microstructures within the a-Si$_{1-x}$Ge$_x$:H films. In SWPM of the rf amplitude by controlling the pulse period and duty cycle of the pulse we could reduce the microstructure factor $R^*$ in the films over the middle composition range of $x$=0.40–0.45. The gradual formation of nanocrystallites with lowering of pulse duty cycle improved the optoelectronic properties of the films. At 75% duty cycle we obtained the best a-Si$_{1-x}$Ge$_x$:H films with high value of $L_d$ of 100 nm.

## Acknowledgments

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