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

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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 $\mu\tau = 1.0\times10^{-6}$ $cm^2\,V^{-1}$.

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 heterogeneity 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 optoelectronic 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

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($\mu\tau$) 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 (σ_{Ph}) to dark conductivity (σ_D) where σ_{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]

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

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 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).

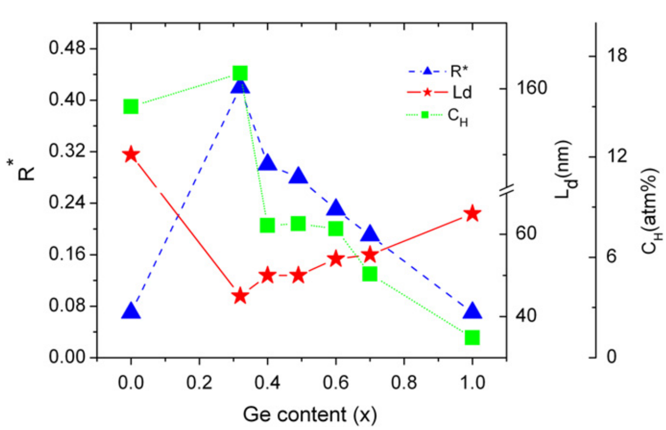

Fig. 1. Evolution of ambipolar diffusion length L_d, IR microstructure factor R^* and hydrogen content C_H with Ge content (x).

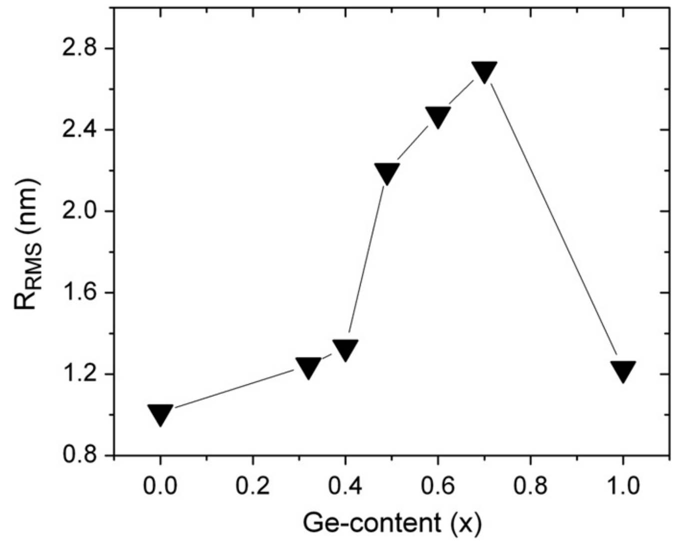

Fig. 2. The RMS surface roughness (R_{RMS}) of the a-Si$_{1-x}$Ge$_x$:H films deposited with various Ge content (x).

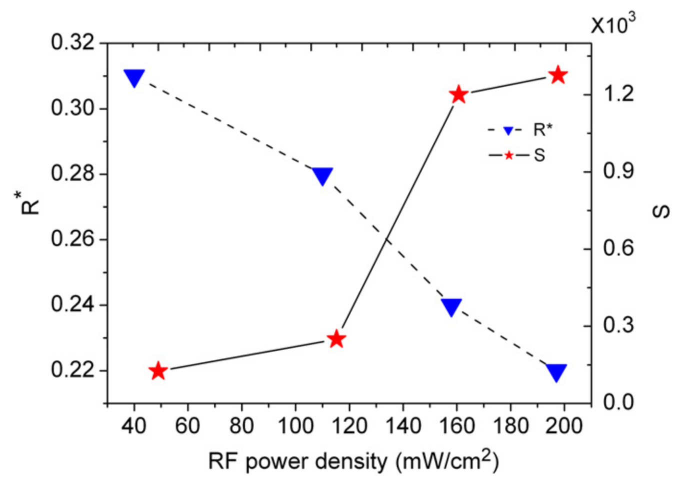

Fig. 3. Evolution of the IR microstructure factor R^* and the photosensitivity S with RF power density variation.

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%.