MICROCRYSTALLINE SILICON-GERMANIUM ALLOYS FOR ABSORPTION LAYERS IN THIN FILM SOLAR CELLS

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ABSTRACT

Thin microcrystalline silicon-germanium films (μc-$Si_{1-x}Ge_x$:H) prepared by PECVD at 95 MHz have been investigated. The optical absorption of these films increases in the infrared spectral region with increasing germanium content. In addition to the shift of the indirect gap an increase of the absorption coefficient above the band edge is observed. The material shows high crystallinity and exhibits good structural quality similar to pure μc-Si:H films. The films are homogeneous on a macroscopic to a microscopic scale as confirmed by Raman spectroscopy and Electron Microscopy methods. p-i-n solar cells with μc-$Si_{1-x}Ge_x$:H i-layers have been prepared for the first time. An efficiency of $\eta = 3.1$ % under AM1.5 has been obtained for a cell with 150 nm thin i-layer.

INTRODUCTION

For the application as low gap material in stacked solar cells or color sensors a-Si:Ge:H alloys have been developed in the past years with considerable success [1, 2]. Still, due to the inherent instability of a-Si:Ge:H, alternative low gap materials were looked for and recently μc-Si:H was proposed and used as low gap material in thin film devices [3, 4]. However, μc-Si:H is an indirect semiconductor with low absorption in the energy range of interest, films of some μm thickness are required for solar cell applications. It is therefore of interest to investigate, in how far, μc-Si:Ge:H alloys can overcome these restrictions of the μc-Si:H. This is motivated by the fact that crystalline (or polycrystalline) SiGe alloys are well known materials with reduced band gap and altered band structure leading to changes of the interband absorption with respect to crystalline silicon [5, 6]. From this changes a shift of the indirect gap and an increase of the absorption coefficient above the band edge is expected also in the microcrystalline alloys. While microcrystalline silicon-germanium alloys (μc-Si:Ge:H) have already been prepared during the development of amorphous SiGe alloys, e.g. [7] only very recently such films have been considered as candidate for low gap absorption layers [8].

In the present study very high frequency (VHF) glow discharge is used to prepare μc-Si:Ge:H films of different composition. The VHF glow discharge technique has been used to improve the material quality and the growth rate of μc-Si:H [9]. The growth rate is one of the most crucial issues with respect to commercialization. Optical absorption spectroscopy and structural investigations by Raman spectroscopy and Electron Microscopy methods are used to characterize the samples and the results are compared with literature data for (poly-) crystalline SiGe alloys. Furthermore, we present the first results on p-i-n solar cells with μc-$Si_{1-x}Ge_x$:H as absorption layers of different band gap.

EXPERIMENT

The μc-$Si_{1-x}Ge_x$:H films and the solar cells were prepared by PECVD in a 6-chamber deposition system with base pressure < 10^{-9} mbar at a plasma excitation frequency of 95 MHz at 200 °C substrate temperature [10]. Mixtures of germane (GeH_4) and silane (SiH_4) or disilane Si_2H_6

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diluted in H_2 were used. For structural characterization Raman spectroscopy in a near-back-scattering configuration at λ_o = 488 nm was employed. In addition, (High Resolution) Transmission Electron Microscopy, (HR)-TEM, high resolution Energy Dispersive X-ray emission, HR-EDX, and XRD was used for selected films. Thermally crystallized a-$Si_{1-x}Ge_x$:H films and c-$Si_{1-x}Ge_x$ grown by MBE served as reference material. The germanium concentration in the film was determined by secondary ion mass spectroscopy using Cs^+ ions and detecting $^{28}Si^{133}Cs^+$ and $^{74}Ge^{133}Cs^+$ ions, respectively [11]. The absorption coefficient $\alpha(E)$ is determined from PDS- and simultaneous transmission measurements which yields interference free absolute values [12]. Solar cells were deposited on glass coated with textured TCO (Asahi 'U' type) and consist of a stack glass / TCO / <p> μc-Si:H / μc-$Si_{1-x}Ge_x$:H / <n> a-Si:H/ silver. The cells were characterized by I-V curves under AM1.5, 100 mW/cm^2 and Differential Spectral Response (DSR) measurements.

RESULTS

Preparation

We started with deposition conditions well suited for μc-Si:H growth, i.e. (SiH_4 + GeH_4) / H_2 ≈ 2-5 %, at low power and low pressure. Under these conditions, a transition to amorphous film growth is obtained at about 6 % [10]. With increasing GeH_4 gas flow ratio, the transition to amorphous film growth shifts to higher hydrogen dilution, e.g. the films are amorphous at (SiH_4 + GeH_4 + H_2) / H_2 ≈ 2.5 % and become fully microcrystalline at 1.25 %. When SiH_4 is replaced by Si_2H_6 this value has to be even lower, e.g. 0.6 % for the same Si_2H_6 / GeH_4 ratio. A further increase of the GeH_4 flow does require even higher hydrogen dilution which was not achievable with Si_2H_6 and GeH_4 in our deposition system. Therefore, fully microcrystalline films with the highest germanium content (x ≈ 0.8) could only be achieved with SiH_4 + GeH_4. The results suggest that under the deposition conditions chosen the germane in the gas phase or the germanium in the film inhibits crystalline growth.

Deposition rates between 0.6 Å/s - 1.7 Å/s have been achieved for μc-$Si_{1-x}Ge_x$:H growth. Although the process is not optimized yet, this is more than a factor of 5 higher than reported by [8] and points to the advantage of VHF also for the μc-Si:Ge:H alloy deposition.

Structure and Composition

In Fig. 1 Raman spectra of three μc-$Si_{1-x}Ge_x$:H films with the indicated composition are compared with a c-$Si_{1-x}Ge_x$ film grown by MBE. The Raman spectra show no signal of an amorphous phase. For the purpose of the following only the three strong peaks are considered which are attributed to Si-Si- (~ 500 cm^{-1}), Si-Ge- (~ 450 cm^{-1}), Ge-Ge-(~ 300 cm^{-1}) optical modes according to [13]. In the microcrystalline films the peaks are broadened by about a factor of 2 (3) when compared with the MBE sample (polycrystalline SiGe [14]) at a similar composition. The larger width of the Raman spectra can either be due to a larger disorder, a strain distribution in the microcrystalline films, or due to size effects of small crystallites. As the weak extra peaks between 430 cm^{-1} and 475 cm^{-1}, which are attributed to Si-Si modes localized by disorder [15], are much stronger than in random alloys, we suspect an increased disorder in our films. The absence of a peak at 520 cm^{-1} in all microcrystalline samples shows that no silicon clusters are formed and no indication for a phase separation is found (note that the weak Raman peak at 520 cm^{-1} in the MBE sample is due to the substrate).

In Fig. 2 the peak position of the Raman optical modes is shown as a function of the

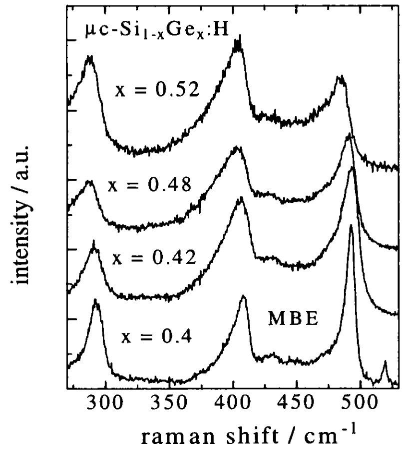

Fig. 1: Raman spectra of μc-$Si_{1-x}Ge_x$:H with indicated composition

composition x and compared with data from the literature [14, 15]. For the medium composition range the Si-Si mode falls nicely on the straight line suggested from the literature data. Small deviations occur at higher Ge-content which could be due to the interference with disorder induced Raman peaks or due to strain. Similarly, the Si-Ge mode follows the trend of the (poly-) crystalline data, and the agreement is still reasonably good. For the Ge-Ge mode a linear dependence of the peak position on the Ge-content is suggested from the (poly-) crystalline data. The observed deviations of the peak position of the microcrystalline films from the straight line are of similar magnitude as for the data on Liquid Phase Epitaxy material [15]. Note the different scale which leads to a larger scatter of the Si-Ge and Ge-Ge data. All Raman data show only very small changes when scanned across the sample.

Dark and bright field TEM images reveal a microstructure similar to μc-Si:H. When grown on amorphous substrate, the microcrystallites start with a cone-like shape which are slightly smaller than in μc-Si:H at the same plasma excitation frequency. The cones are embedded in an amorphous transition zone of about 20 nm. The crystallites extend over the whole film thickness. High resolution images show structural defects such as stacking faults and twins within the crystallites. The composition of the films on a scale < 6 Å has been investigated by HR-EDX in lateral direction and in the direction of film growth. It turns out, that the amorphous phase at the interface as well as the crystallites are homogenous, i.e. the composition varies by less than +/- 2 % when the analysis is made over the whole film thickness.

Thus, from structural investigations the following conclusion can be drawn: Using VHF deposition μc-$Si_{1-x}Ge_x$:H films of high crystalline volume fraction and good structural quality can be prepared. No phase separation is observed and the samples show good homogeneity of the composition on a macroscopic scale. The Raman line width is dominated by disorder. The position of the Si-Si optical mode is a good measure of the Ge-content in the film. TEM and HR-

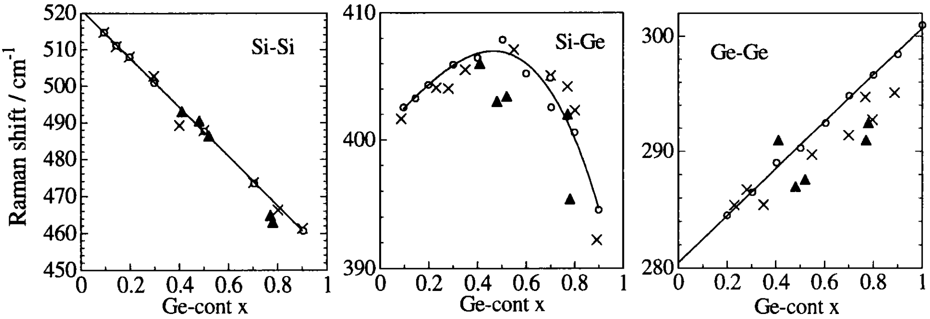

Fig. 2: Peak position of the indicated Raman modes as a function of the Ge-content. Circles are from ref. [14], crosses from ref. [15] and triangles from μc-Si:Ge:H films of this study

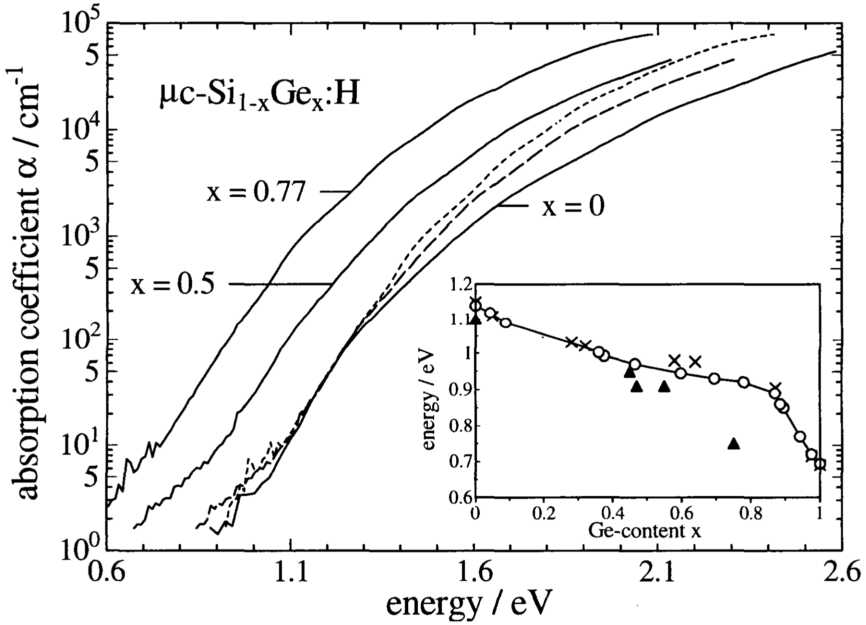

Fig. 3: Optical absorption spectra for different composition. Insert: optical gap as function of Ge-content (see text for details)

EDX investigations show that the films are homogeneous on a nm scale and microstructure is similar to μc-Si:H, i.e. the films have a columnar structure with crystallites that start cone shaped at the interface embedded in an amorphous matrix. Therefore, the films look similar to μc-Si:H prepared at lower frequency and/or lower hydrogen dilution.

Optical properties

Optical absorption spectra evaluated from PDS and transmission spectra are shown in Fig. 3 for 3 samples covering the investigated composition range. In the insert the optical gap of the μc-Si$_{1-x}$Ge$_x$:H films (Δ) and (poly-)crystalline Si$_{1-x}$Ge$_x$ taken from [5] (X) is shown. In both cases the gap has been defined as $\alpha(E_g) = 10\ \mathrm{cm}^{-1}$ which is close to the indirect gap. This was necessary because a plot of $\sqrt{\alpha}$ as a function of E does not always give straight lines over a reasonable energy range. In addition, the energy of the 0-phonon line of photoluminescence spectra at 4.2 K is given (o), which can also be used to define a optical gap [13]. It is obvious that the gap of the μc-Si$_{1-x}$Ge$_x$:H films is only slightly narrower than the corresponding (poly-)crystalline material for Ge-content up to x = 0.55. In contrast, the film with x = 0.77 show a much narrower gap by 0.2 eV. Such a strong shift is expected only at higher Ge-content. At such high Ge-contents a change of the shape of the absorption curve is found in (poly-)crystalline material. Instead, the absorption spectrum of the microcrystalline film looks similar to those of smaller Ge-content. We have carefully checked the x = 0.77 sample on its Ge-content with SIMS and for a change of the gross film structure on phase separation by Raman spectroscopy but we can rule out either effect.

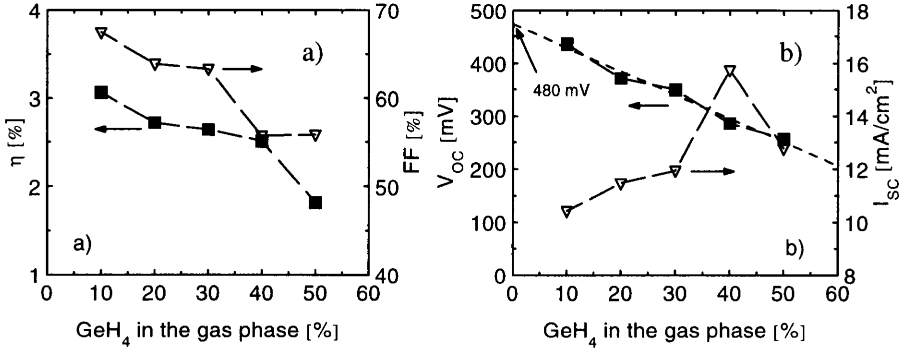

Fig. 4: a) efficiency η and fill factor FF, b) open circuit voltage V_{OC} and short circuit current I_{SC} of pin solar cells with 150 nm thick μc-Si:Ge:H i-layers prepared with different GeH_4 content in the gas phase.

In addition to the shift of the gap we find an increase of the absorption above the gap. This is demonstrated in Fig 3 where the spectra of the two μc-$Si_{1-x}Ge_x$:H films are shifted vertically by 0.17 eV for $x = 0.5$ (long dash) and 0.32 eV for $x = 0.77$ (short dash). The increase of the absorption coefficient with increasing Ge-content is obvious, e.g. at 1 eV above the band gap the absorption coefficient is enhanced by about a factor of 2 for $x = 0.5$ and a factor of 3 for $x = 0.77$. This effect can be particularly advantageous when thin films are used.

μc-Si:Ge:H pin solar cells

To prove whether the p-i-n concept will work with this new absorber material, solar cells with very thin μc-Si:Ge:H i-layers (150) nm with different GeH_4 content in the gas phase were prepared. In Fig. 4 a-b the cell parameters efficiency η, open circuit voltage V_{OC}, fill factor FF, and short circuit current I_{SC} obtained from I/V curves under AM1.5 conditions are shown as a function of GeH_4 . From the measurement on films we expect the germanium content in the i-layer similar to that of GeH_4 in the gas phase. For the V_{OC} we observe a decrease with increasing GeH_4 content in the gas phase. This decrease is stronger than the decrease expected from the band gap reduction of the i-layer material due to Ge alloying from about 1.05 eV for 10% GeH_4 down to 0.9 eV for 50% GeH_4 (see Fig. 4). The reason for this behavior is not clear. Extrapolation to a GeH_4 content of 0% gives 480 mV, which is typically obtained for μc-Si:H cells [3, 16]. FF values up to 67% were reached for low GeH_4 contents, whereas for GeH_4 contents higher than 30% the FF drops down to 55%. This points to a reduced carrier collection due to poor material quality or problems in the cell design, e.g. band gap discontinuities at the p/i and i/n interface regions. An increase of I_{SC} with increasing GeH_4 content is observed exceeding 16 mA/cm^2 at 40% GeH_4 due to a higher absorption coefficient in the i-layer material at lower band gap. For higher GeH_4 content the carrier collection is reduced due to the problems mentioned above. The highest efficiency of a μc-Si:Ge:H pin solar cell so far is 3.1 % and is obtained for the cell with the lowest germanium content. The spectral response of the cells extend to λ > 1000 nm and show the expected enhancement in the near infrared with increasing Ge-content.

SUMMARY

μc-$Si_{1-x}Ge_x$:H films of good structural and optoelectronic properties have been prepared by VHF glow discharge with encouraging high deposition rates. The composition and the structure of the films is homogeneous besides a thin amorphous transition layer when grown on amorphous substrates. An enhanced absorption in the near infrared is observed which is due to a shift of the band gap and an enhanced absorption due to the modified band structure of the alloys. p-i-n solar cells with μc-$Si_{1-x}Ge_x$:H i-layer show a linear decreasing V_{OC} and a decreasing fill factor with increasing Ge-content. I_{SC} increases with increasing Ge-content as expected from the higher absorption coefficient but seems limited by the deterioration of the film quality. The highest efficiency obtained under AM1.5 was 3.1 %. The results obtained so far are encouraging and show that μc-$Si_{1-x}Ge_x$:H is a promising material for low gap solar cells.

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