# Deposition of $\mu$ c-Si and $\mu$ c-Si–C thin films by remote plasma-enhanced chemical-vapor deposition

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#### Abstract

This paper describes properties of microcrystalline silicon ( $\mu$ c-Si), and microcrystalline silicon–carbon ( $\mu$ c-Si–C) thin films formed by the process of remote plasma-enhanced chemical-vapor deposition (PECVD). We discuss: (i) the way that the remote PECVD deposition process is applied to the deposition of  $\mu$ c-Si and  $\mu$ c-Si–C thin films; (ii) the characterization and properties of the intrinsic and doped  $\mu$ c-Si thin film materials; (iii) the characterization and properties of the intrinsic and doped  $\mu$ c-Si–C thin film materials; and (iv) the application of remote PECVD  $\mu$ c-Si and  $\mu$ c-Si–C thin films in device structures.

## 1. Introduction

The glow discharge (GD) deposition process has become the standard technology for the deposition of thin films of hydrogen-doped amorphous silicon (a-Si:H) and its alloys with carbon and germanium, a-Si-C:H and a-Si-Ge:H. respectively, in the fabrication of thin film devices, including p-i-n solar cells and thin film transistors (TFTs). It is also the standard technology for the deposition of doped microcrystalline-silicon ( $\mu$ c-Si), and doped  $\mu$ c-Si-C alloys, that are also utilized in p-i-n solar cells. The electrical properties of undoped or "intrinsic"  $\mu$ c-Si as deposited by the GD process are not adequate for the i layers in photovoltaic (PV) devices or the channel layers in TFT devices, and as such have received little attention. For example, undoped  $\mu$ c-Si deposited by the GD process usually has a relatively high conductivity,  $> 10^{-2}$  S cm<sup>-1</sup>, and a relatively high density of defect states at mid-gap, about  $10^{18}$  cm<sup>-3</sup> eV [1]. In addition,  $\mu$ c-Si thin films deposited by the GD process frequently have a significant region of non-crystalline silicon between the deposition substrate and the onset of the  $\mu$ c-Si material. The structure of this transitional region has not been fully characterized, either structurally or electronically; however, in most instances, it is an a-Si:H film with a thickness of at least 100 Å, and frequently as large as 500–1000 Å. Under some conditions of deposition, a similar transition region has also been found in thin films of  $\mu$ c-Si deposited by reactive magnetron sputtering [2, 3].

In this paper, we describe a new technique for the deposition of  $\mu$ c-Si and  $\mu$ c-Si-C alloys, namely r.f.-excited remote PECVD [4, 5]. Using this

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deposition process, thin films of  $\mu$ c-Si and  $\mu$ c-Si–C alloys can be deposited at substrate temperatures between 100 and 400  $^{\circ}$ C, and on a variety of different substrate materials, including a-Si, crystalline silicon and thermally grown, or plasma-deposited SiO<sub>2</sub>. This has been accomplished using hydrogen dilution of the silicon source gas with two different deposition reactions; one which uses remote plasma excitation of helium-hydrogen mixtures with downstream injection of the source gases including SiH<sub>4</sub>, as well as any alloy, or dopant gases, e.g. CH<sub>4</sub>, PH<sub>3</sub> or B<sub>2</sub>H<sub>6</sub>, respectively; and one which uses remote plasma excitation of helium, with downstream injection of hydrogen, as well as the  $SiH_4$ ,  $CH_4$  and any dopant atom source gases. We have observed that deposition by the second pathway, in which the hydrogen is introduced downstream, consistently results in the formation of homogeneous  $\mu$ c-Si films with no detectable non-crystalline or amorphous silicon transition region between the substrate and the deposited thin films. The limit of detection for such a transition layer is about 30 Å, as determined from transmission electron microscopy (TEM) micrographs. Using reactive magnetron sputtering from a silicon target in a hydrogen and argon ambient,  $P_{\rm H} = 0.4$  mTorr, and  $P_{\rm Ar} = 2.0-4.0$  mTorr, where  $P_X$  is the partial pressure of the gas X, we have previously reported the observation of an a-Si "transition" layer between the substrate and the onset of a  $\mu$ c-Si material for films deposited at substrate temperatures in excess of about 500 °C [6]. For samples deposited at lower substrate temperatures, e.g. 250 °C, but with higher partial pressures of hydrogen,  $P_{\rm H} = 4.0$  mTorr, we have also obtained  $\mu$ c-Si thin films, but this time with no detectable non-crystalline transition region between the substrate and the onset of the  $\mu$ c-Si layer.

We first describe the remote PECVD process, and in particular the way that it has been used for the deposition of  $\mu$ c-Si and  $\mu$ c-Si–C thin films. We then discuss the structural, chemical and electronic properties of the undoped and doped thin film materials. Finally, we indicate the results of experiments in which these thin film materials have been incorporated into device structures that include p–i–n diodes, *i.e.* PV device structures.

## 2. Deposition of $\mu$ c-Si by remote PECVD

## 2.1. The remote PECVD process

The remote PECVD process was originally developed for the deposition of silicon-based dielectrics such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> [7, 8], and has also been applied for the deposition of a-Si:H thin films [9]. The detailed design of the chambers used for this deposition process are discussed elsewhere [10, 11]. This paper focuses on the extension of the remote PECVD process to the deposition of  $\mu$ c-Si and  $\mu$ c-Si–C thin films. For the deposition of a-Si and  $\mu$ -Si, the principal difference between remote PECVD and the conventional GD process is in the plasma activation processes for the silicon and the dopant source gases.

In the GD process, all source gas molecules are subjected to direct plasma excitation, and are broken up in the gas phase generating chemically reactive deposition precursor species which are "fragments" of the source gas molecules. For example, when the silicon source gas molecule is  $SiH_4$ , these fragments include neutral and charged SiH<sub>3</sub>, SiH<sub>2</sub>, SiH, silicon and atomic hydrogen. In contrast, in the remote PECVD process, the silicon and dopant atom source gases are remotely excited by the species transported out of a noble gas plasma, usually helium, and are not fragmented in the gas phase. The active species initiating downstream activation of the  $SiH_4$ are primarily low energy electrons (<10 eV), and also possibly noble gas ions and metastables. The remote PECVD process takes place in four separate steps: (i) the remote plasma excitation of the helium; (ii) the extraction and transport of active species - electrons, helium ions and helium metastables - from the plasma generation region and into the deposition region; (iii) the mixing of these plasma-generated species with  $SiH_4$ , and alloy atom and/ or dopant source gases resulting in excitation of these molecules either in the gas phase, or at the deposition substrate; and (iv) the deposition of a film on a heated substrate that is outside the plasma generation region. For the deposition of device-quality undoped and doped a-Si:H films, the remote PECVD process is typically carried out at a chamber pressure of about 300 mTorr, a plasma power between 15 and 50 W, and with helium flow of a 200 standard cubic centimeters per minute (sccm) through the plasma tube. The flow rate of the SiH<sub>4</sub> is about 1 sccm, and the SiH<sub>4</sub> is diluted about 9:1, usually with helium. Doped a-Si films are produced by adding small quantities of either  $PH_3$  or  $B_2H_6$  to the  $SiH_4$  source gas, and then subjecting the  $SiH_4$  and dopant atom source gases to remote excitation as described above. The effectiveness of the doping process, as measured by the conductivity or activation energy, for a given ratio of dopant gas to  $SiH_4$ , is the same for films produced by the remote PECVD as for films produced by the GD process where the SiH<sub>4</sub> and dopant gases are directly plasma excited. The combination of the flow rates of helium through the plasma tube, and silicon and dopant atom source gases through the downstream showerhead injection rings, coupled with the process pressure of about 300 mTorr in the deposition region of the chamber, prevents any significant backstreaming of the reactant process gases into the plasma generation region. This effectively eliminates any gas phase fragmentation of the  $SiH_4$ , and thereby also restricts the number of simultaneous deposition reaction pathways.

Using the remote PECVD technique, we have deposited device- or PVgrade undoped and doped a-Si:H, and have also fabricated discrete a-Si:H, TFTs, and TFT circuits employing up to six transistors [10, 12, 13]. The main difference in chemical composition between a-Si:H films produced by remote PECVD and by the GD process for substrate temperatures between 100 and 400 °C, is in a lower concentration of bonded hydrogen in the remote PECVD films. The remote PECVD films typically have a factor of two less hydrogen over a significant portion of this range, *e.g.* from about 150 °C to about 250 °C. Since device-quality a-Si:H can not have a bonded hydrogen concentration in excess of about 20 at.%, this difference in bonded hydrogen concentrations means that PV-quality, intrinsic and doped a-Si:H can be deposited by remote PECVD at temperatures as low as 150 °C, in contrast to the temperatures required for PV-grade films deposited by the GD process (about 220 °C to about 250 °C) [14]. Implicit in this observation is the fact that for substrate temperatures in excess of 150 °C, there is sufficient annealing, during film deposition by the remote PECVD process, to remove any defects associated with the film formation process. The a-Si:H films produced by the remote PECVD process have electrical properties that are essentially the same as the GD films. For example, the PV-quality undoped films have photoconductivities and sub-band gap optical absorption constants that are the same as those of PV-quality GD films. In addition the remote PECVD films display the same rates of defect formation by light-soaking.

# 2.2. Deposition of $\mu$ c-Si thin films

It has also been reported that  $\mu$ c-Si films can be deposited at low substrate temperatures, 150 °C <  $T_{\rm s}$  < 450 °C, using the GD deposition process by simply adding a large amount of hydrogen to the gas mixture, *e.g.* H<sub>2</sub>/ SiH<sub>4</sub> > 50:1 [15]. It has been proposed that strong hydrogen dilution in the gas phase promotes near-equilibrium chemical reactions at the substrate that slow down the deposition rate from more than 2–5 Å s<sup>-1</sup> to less than 0.5 Å s<sup>-1</sup>, permitting the nucleation of the microcrystallites [16].

We also used high hydrogen dilution to deposit  $\mu$ c-Si films by remote PECVD. Dilution with variable concentrations of hydrogen was accomplished in two different ways; (i) by the plasma excitation of He–H<sub>2</sub> mixtures with downstream injection of SiH<sub>4</sub>, and the dopant gases; and (ii) by plasma excitation of helium, with downstream injection of hydrogen, SiH<sub>4</sub> and the dopant gases. Dilution ratios were in the range of 5:1 to 80:1 [4]. The structure of the deposited films was studied by Raman scattering, and the film structure, and its interface with various substrates, were studied by TEM micrographs.

We also deposited a-Si-C:H and  $\mu$ c-Si-C alloys by remote PECVD. The a-Si-C:H alloys were deposited by remote excitation of SiH<sub>4</sub>-CH<sub>4</sub> mixtures, where the source gas ratio  $x = \text{SiH}_4/(\text{SiH}_4 + \text{CH}_4)$  was varied from 1.00 to 0.33. We initially deposited undoped and p-type a-Si-C:H alloy films, and characterized them by IR analysis and by determining their electrical conductivity, photoconductivity and band gaps. We then modified the process by the addition of hydrogen and determined the conditions necessary for formation of undoped and doped  $\mu$ c-Si-C alloy films, but only for one source gas ratio, x = 0.67.

#### 3. Properties of $\mu$ c-Si thin films

Figure 1 is a TEM micrograph of a  $\mu$ c-Si–SiO<sub>2</sub> multilayer structure. All of the films were deposited at 250 °C. The SiO<sub>2</sub> layers were deposited with plasma excitation of a helium–oxygen mixture with respective flow rates of



Fig. 1. TEM micrograph of a  $\mu$ c-Si-SiO<sub>2</sub> multilayer structure. All films,  $\mu$ c-Si as well as SiO<sub>2</sub>, were deposited at  $T_s = 250$  °C. Different concentrations of hydrogen, corresponding to H<sub>2</sub>/SiH<sub>4</sub> ratios of 10:1, 30:1 and 50:1, were injected either upstream or downstream. The layers marked 1, 2 and 3 are for upstream injection of hydrogen for H<sub>2</sub>/SiH<sub>4</sub> ratios of 50:1, 30:1 and 10:1, respectively; and those marked 4, 5 and 6 are downstream injection of hydrogen for H<sub>2</sub>/SiH<sub>4</sub> ratios of 10:1, 30:1 and 50:1, respectively.

200 sccm and 20 sccm. SiH<sub>4</sub> was injected downstream at a flow rate of 1 sccm; the SiH<sub>4</sub> was diluted 9:1 in helium, so that the total flow rate of the downstream injected mixture was 10 sccm. The  $\mu$ c-Si layers were deposited at the same substrate temperature, and using the same flow rate of helium, and diluted SiH<sub>4</sub>, but with the oxygen flow reduced to zero. In addition, for the deposition of the  $\mu$ c-Si layers, hydrogen was introduced in two ways; it was either injected upstream, and plasma excited along with the helium; or injected downstream, and remotely excited along with the silicon and dopant atom source gases. For both of these methods, the hydrogen flow rate was varied between 5 and 80 sccm, corresponding to  $H_2/SiH_4$  ratios between 5:1 and 80:1. The micrograph contains data for flow rate ratios between 10:1 and 50:1. For these flow rate ratios, the deposited films were microcrystalline as evidenced by the micrographs in Fig. 1, and the Raman scattering data of Figs. 2 and 3. The Raman scattering data are discussed in more detail below. A 5:1 flow rate ratio gave an amorphous film, whereas higher ratios (studied up to 80:1) gave  $\mu$ c-Si films. The crystallite size was typically in range 50–100 Å, and did not vary much with the  $H_2/SiH_4$  ratio. However, the crystallite sizes in the  $\mu$ c-Si films deposited with downstream-injected hydrogen were generally larger than those in the films deposited with upstreaminjected hydrogen. In addition, there is no evidence in Fig. 1 for the formation of any significant transition region of a-Si between the  $SiO_2$  layers and the onset of the deposition of the  $\mu$ c-Si thin films. In order to examine this more closely, we performed TEM (Fig. 4) and Raman (Fig. 5) measurements on a sandwich cell sample that consisted of a crystalline germanium substrate, a thin film of SiO<sub>2</sub>, and then the  $\mu$ c-Si. The thickness of the thin film SiO<sub>2</sub> was adjusted to provide a condition for electric field enhancement in the  $\mu$ c-Si thin film material, *i.e.* the optical path length in the film was set at



Fig. 2. Raman spectra of  $\mu$ c-Si films deposited at  $T_s$ =250 °C, with variable flows of hydrogen injected downstream.

 $\lambda/4$  for the Raman scattering laser wavelength. Under these conditions we could obtain Raman spectra for film thicknesses down to about 100 Å. From the combination of Raman scattering measurements in Fig. 5, and TEM micrograph shown in Fig. 4, we estimate that there is at most a 20–30 Å layer of non-crystalline silicon between the thin film and the  $\mu$ c-Si layer.

The corresponding Raman spectra of the  $\mu$ c-Si films of Fig. 1 are shown in Figs. 2 and 3 [5]. In all cases the substrate temperature is 250 °C, and the flow rate of  $SiH_4$  is fixed at 1 sccm; the deposition variable is the flow rate of the hydrogen gas, which is injected downstream in Fig. 2, and upstream with the helium in Fig. 3. The spectra in these figures demonstrate that the transition between deposition of amorphous and microcrystalline films is driven by changing the hydrogen flow rate. The spectrum at the bottom of Fig. 5 is indicative of a-Si:H, as evidenced by the broad spectral features centered at about 150  $cm^{-1}$  and 470  $cm^{-1}$ . The relatively sharp feature at about 520 cm<sup>-1</sup> in films deposited with H<sub>2</sub>/SiH<sub>4</sub> ratios greater than 10:1 is the spectral signature of  $\mu$ c-Si. The degree of microcrystallinity is determined from two factors; (i) the ratio of the scattering intensity at the spectral peak of the sharp  $\mu$ c-Si feature, to the scattering at about 470 cm<sup>-1</sup>; and (ii) the width of the  $\mu$ c-Si feature. The spectrum with the strongest and sharpest microcrystalline feature was obtained for a flow rate of 30 sccm of hydrogen introduced downstream, and for  $T_s = 250$  °C. There is an additional correlation between the TEM micrographs and the Raman spectra that also establishes an overall "microcrystalline quality" factor for the  $\mu$ c-Si thin films; this is in the approximate size and volume fraction of the microcrystallites. Based



Fig. 3. Raman spectra of  $\mu$ c-Si films deposited at  $T_s = 250$  °C, with variable flows of hydrogen injected upstream.



Fig. 4. TEM micrograph of crystalline Ge–SiO<sub>2</sub>– $\mu$ c-Si structure.

on this combination of Raman scattering spectra and TEM micrograph data, we have focused the remainder of our study of films deposited at 250 °C with a  $30:1 \text{ H}_2/\text{SiH}_4$  ratio, with the hydrogen being injected downstream.

All of the Raman spectra for the  $\mu$ c-Si films also show a secondary feature at about 490 cm<sup>-1</sup> in addition to the sharp crystalline feature at about 520 cm<sup>-1</sup>. This feature is not at a frequency characteristic of a-Si, but is also too broad to be a feature associated with the crystalline material. There are two possibilities for its presence in the films: (i) it is a signature



Fig. 5. Raman spectra of crystalline Ge–SiO<sub>2</sub>– $\mu$ c-Si structure for  $\mu$ c-Si film thicknesses from 100 to 2500 Å. The lower trace is the Raman spectrum for the Ge–SiO<sub>2</sub> structure, with no  $\mu$ c-Si.

of the non-crystalline silicon material that is between the microcrystallites; or (ii) it is characteristic of a thin non-crystalline interfacial region between the substrate and the deposited  $\mu$ c-Si film. To determine whether this amorphous feature came from the film bulk, or the interface between substrate and  $\mu$ c-Si film, we deposited a series of different thickness  $\mu$ c-Si films and measured their Raman spectra using the resonance-enhanced method [17]. To eliminate any features from the substrate in the vicinity of 400 to 500  $cm^{-1}$ , we used a single crystal germanium substrate. We deposited about 400 Å of  $SiO_2$  onto the germanium; this formed the resonant structure that maximized the electric field of the incident laser at the  $\mu$ c-Si films that were then deposited onto the SiO<sub>2</sub>. Five  $\mu$ c-Si films with different thicknesses ranging from about 100 Å to about 2500 Å were then deposited on top of the SiO<sub>2</sub> with  $T_s = 250$  °C using 30 sccm hydrogen introduced downstream. The relevant Raman spectra are shown in Fig. 5. Note that the film thickness was increased incrementally, and the Raman spectrum was measured after deposition of  $\mu$ c-Si. The corresponding micrograph, shown in Fig. 4, was made after all the  $\mu$ c-Si depositions were completed. The micrograph indicates a relatively abrupt interface between the  $SiO_2$  and the microcrystalline silicon deposits; however, one cannot completely rule out a transition region of silicon with a non-crystalline character, and having a thickness of less than about 30 Å. Returning to the Raman spectra, we find that the sharp feature,

at about 520 cm<sup>-1</sup>, dominates in all of the spectra, even in the thinnest  $\mu$ c-Si film of 100 Å. All the films also show some additional scattering in between about 490 cm<sup>-1</sup> and about 500 cm<sup>-1</sup>. In addition, the 100 Å sample shows some additional scattering below about 490  $\text{cm}^{-1}$ . Using these data, we interpret the scattering between about 490 cm<sup>-1</sup> and 500 cm<sup>-1</sup> as being due to the non-crystalline material in the bulk of the  $\mu$ c-Si thin films, *i.e.* it is associated with the material that lies between the silicon microcrystallites. This interpretation is based on the observation that the ratio of the scattering at the spectral peak at 520  $\text{cm}^{-1}$  to the scattering at 490  $\text{cm}^{-1}$  is essentially independent of film thickness. In contrast, the scattering below about 485  $cm^{-1}$  is strongest in the thinnest film, 100 Å thick, and is assumed to be associated with a thin (<30 Å) interfacial region of a-Si:H that is present between the  $\mu$ c-Si film and the SiO<sub>2</sub> substrate. There is some evidence for such a region in the micrograph. However, it should be noted that an a-Si:H region with a thickness of <30 Å, would not interfere in most of the device applications being considered for  $\mu$ c-Si.

We have also studied the deposition of doped  $\mu$ c-Si using the same remote PECVD process discussed above; *i.e.* downstream injection of all gases except for helium, a flow ratio of H<sub>2</sub>:SiH<sub>4</sub> of 30:1 and a substrate temperature of 250 °C. By remotely exciting mixtures of PH<sub>3</sub>-SiH<sub>4</sub> or B<sub>2</sub>H<sub>6</sub>-SiH<sub>4</sub>, respectively, n-type and p-type  $\mu$ c-Si films were obtained. The undoped  $\mu$ c-Si has a dark conductivity of  $\approx 6 \times 10^{-4}$  S cm<sup>-1</sup>, and a dark conductivity activation energy of 0.33 eV (Table 1). The dark conductivity increases monotonically with the addition of PH<sub>3</sub> to the SiH<sub>4</sub>, and at the same time the dark conductivity activation energy decreases. The highest value of dark conductivity, obtained for a source gas ratio of PH<sub>3</sub>/SiH<sub>4</sub> = 10<sup>-2</sup>, was 40 S cm<sup>-1</sup>; this sample had a dark conductivity activation energy of about 0.02 eV.

The addition of a relatively small amount of the p-type dopant gas,  $B_2H_6/SiH_4 = 10^{-5}$ , caused a decrease of four orders of magnitude in the dark conductivity to about  $6 \times 10^{-8} \,\mathrm{S \, cm^{-1}}$ , paralleling a similar behavior previously reported for boron-doped a-Si. In addition, a result similar to what we have found in  $\mu$ c-Si, was obtained by LeComber et al. [18], who used ionimplantation instead of a PECVD technique. They did not report on any properties of this material other than the dark conductivity. Returning to the remote PECVD material, the activation energy of the boron-compensated material  $(B_2H_6/SiH_4 = 10^{-5})$  showed an increase in activation energy to 0.7 eV, which is about one-half of the optical gap, 1.44 eV, as defined by  $E_{04}$ , the photon energy at which the optical absorption constant is  $10^4$  cm<sup>-1</sup>. From this, we conclude that the dark conductivity in the undoped  $\mu$ c-Si is defect controlled, and that this lightly boron-doped film is near-intrinsic, in the sense that the Fermi energy is now at mid-gap, rather than closer to the conduction band edge as in the undoped, as-deposited  $\mu$ c-Si films. This means that any donor-like defects of the undoped material have been compensated by the addition of the p-type dopant atom boron. Higher concentrations of  $B_2H_6$  to SiH<sub>4</sub>, between  $10^{-5}$  and up to about  $1 \times 10^{-3}$ ,

Material	H <sub>2</sub> /SiH <sub>4</sub> ratio	Dopant gas/ SiH₄ ratio	Dark conductivity (S $cm^{-1}$ )	Activation energy (eV)
a-Si:H	0	0	$2.4 \times 10^{-10}$	0.80
a-Si:H(n)	0	$1 \times 10^{-2}$	$2.0 \times 10^{-3}$	0.25
a-Si:H(p)	0	$1 \times 10^{-1}$	$2.4 \times 10^{-3}$	0.31
μc-Si	30:1	0	$6.0 \times 10^{-4}$	0.30
$\mu$ c-Si(n)	30:1	$3 \times 10^{-5}$	0.2	0.08
μc-Si(n)	30:1	$3 \times 10^{-4}$	5.0	0.05
$\mu$ c-Si(n)	30:1	$1 \times 10^{-2}$	40	0.018
$\mu c-Si(p)$	30:1	$1 \times 10^{-5}$	$6.0 \times 10^{-8}$	0.70
$\mu c$ -Si(p)	30:1	$2 \times 10^{-4}$	$7.0 \times 10^{-4}$	0.24
$\mu c$ -Si(p)	30:1	$1 \times 10^{-3}$	6.0	0.04
a-Si:H(p)	30:1	$1 \times 10^{-2}$	$4.0 \times 10^{-5}$	0.40
a-Si:H(p)	30:1	$1 \times 10^{-1}$	$3.0 \times 10^{-3}$	0.30
a-Si-C:H	0	0	$2.3 \times 10^{-13}$	0.99
a-Si–C:H(p)	0	$1 \times 10^{-3}$	$2.0 \times 10^{-9}$	0.69
a-SiC:H(p)	0	$1 \times 10^{-2}$	$1.4 \times 10^{-6}$	0.46
μc-Si–C(p)	30:1	$1 \times 10^{-3}$	$6.3 \times 10^{-4}$	0.18
a-Si-C:H(p)	30:1	$1 \times 10^{-2}$	$1.4 \times 10^{-7}$	0.56

 TABLE 1

 Electrical properties of films grown by remote PECVD

N-type samples were deposited from PH<sub>3</sub>-SiH<sub>4</sub> mixtures.

P-type samples were deposited from B<sub>2</sub>H<sub>6</sub>-SiH<sub>4</sub> mixtures.

Si-C alloys were deposited from  $CH_4$ -SiH<sub>4</sub> mixtures with SiH<sub>4</sub>/( $CH_4$ +SiH<sub>4</sub>)=0.33.

produced increases in the dark conductivity, accompanied by decreases in the dark conductivity activation energy (Table 1). The highest level of dark conductivity obtained in p-type  $\mu$ c-Si by remote PECVD was 6 S cm<sup>-1</sup>, with an activation energy of 0.04 eV. Further increases in the ratio of B<sub>2</sub>H<sub>6</sub> to SiH<sub>4</sub> in the feed gas resulted in decreases in the dark conductivity, and increases in the dark conductivity activation energy. These decreases in the dark conductivity resulted from the deposited films being amorphous rather than microcrystalline; this conversion from microcrystalline to amorphous character was determined by Raman scattering spectroscopy.

We have conducted a detailed study of the "most-resistive"  $\mu$ c-Si grown from the B<sub>2</sub>H<sub>6</sub>/SiH<sub>4</sub> = 10<sup>-5</sup> source gas mixture. These films are qualitatively different from the undoped films with regard to their photoconductivity, and have opened up what we believe to be interesting new options for device structures. We have found the following results for the boron-compensated near intrinsic  $\mu$ c-Si: (i) a dark conductivity of  $6 \times 10^{-8}$  S cm<sup>-1</sup> with a dark conductivity activation energy of 0.70 eV; (ii) an effective band-gap as defined by  $E_{04}$  of 1.44 eV; (iii) a monochromatic photoconductivity of  $4 \times 10^{-5}$  S cm<sup>-1</sup> for a generation rate of about  $1 \times 10^{19}$  cm<sup>-3</sup>; (iv) a relatively flat spectral response per absorbed photon between 500 nm and 750 nm; (v) a photoconductivity of about  $1 \times 10^{-4}$  S cm<sup>-1</sup> for 0.5 air mass (AM) 1 light (50 mW cm<sup>-2</sup>); (vi) no detectable Stabler–Wronski effect for light exposures to 50 mW cm<sup>-2</sup> for up to 6 h. With respect to the light-soaking experiments, it should be noted that an exposure of 6 h to 0.5 AM 1 light results in a decrease of a factor of ten in the photoconductivity of a PV-grade a-Si:H thin film.

# 4. Properties of $\mu$ c-Si–C thin films

In order to interpret the properties of the  $\mu$ c-Si–C thin films, we first present a short discussion of the properties of a-Si–C:H films produced by remote PECVD. In particular, we focus on the IR spectra and the p-type doping obtained for B<sub>2</sub>H<sub>6</sub>/SiH<sub>4</sub> source gas ratios greater than 10<sup>-3</sup>. These data, combined with the data presented in the previous section for  $\mu$ c-Si thin films provide a reference for interpretation of the experimental data presented for the  $\mu$ c-Si–C alloy films.

#### 4.1. a-Si-C:H thin films

We deposited a-Si–C:H alloy films at a substrate temperature of 250 °C using remote excitation of a SiH<sub>4</sub>–CH<sub>4</sub> source gas mixture. We varied the methane fraction, and studied the source gas ratio x from 1 to 0.33. The properties of these films are essentially the same as those produced by the GD process for the same source gas ratio. The  $E_{04}$  band-gap and photo-conductivity data are summarized in Fig. 6 which shows that as x decreases from 1 (a-Si:H), the band gap increases, and the photoconductivity decreases. Figure 7 contains IR transmission data for the same series of depositions. The main spectral features to note are: (i) a shift of the SiH stretching frequency from about 2000 cm<sup>-1</sup> in a-Si:H to about 2075 cm<sup>-1</sup> in all of the a-Si–C:H alloy films; (ii) the appearance of features associated with CH<sub>3</sub>, at about 1250 to about 1400 cm<sup>-1</sup>, and about 2800 to about 3000 cm<sup>-1</sup> in all of the a-Si–C:H alloys; and (iii) the appearance of a sharp feature at about 750 cm<sup>-1</sup> associated with Si–C vibrations, and in a local bonding



Fig. 6.  $E_{04}$  and photoconductivity in a-Si-C:H alloys deposited by remote PECVD.



Wavenumber (cm<sup>-1</sup>) Fig. 7. IR transmission of a-Si-C:H alloys for different ratios of x from 1.0 to 0.33.

environment in which the carbon atom is part of a methyl group, *i.e.* bonded to three hydrogen atoms as in an Si $-CH_3$  structure.

We have also been able to add  $B_2H_6$  downstream to the SiH<sub>4</sub>-CH<sub>4</sub> source gas mixture and produce p-type alloy films. These studies were restricted to x = 0.67. The results of these doping studies are included in Table 1. For the highest doping gas ratio used, the conductivity is about a factor of 500 less than in a-Si:H, and the activation energy is about 0.15 eV higher. These changes are consistent with the prefactor, which is the product of a density of states  $n_b$ , and a band mobility  $\mu_b$ , being essentially the same in the a-Si:H and a-Si-C:H materials; *i.e.*  $\sigma = n_b \mu_b e \exp(-E_a/kT)$ , where  $E_a = E_b - E_f$ ;  $E_b$  is the band edge position, and  $E_f$ , the Fermi energy.

#### 4.2. $\mu c$ -Si-C thin films

We deposited films of  $\mu$ c-Si–C by remote PECVD by adding hydrogen to the downstream injected SiH<sub>4</sub>–CH<sub>4</sub> source gas mixture. For these studies the combined flow rate of this source gas mixture was 1 sccm, and the flow rate of hydrogen was 30 sccm, the same ratio used for the studies of the  $\mu$ c-Si films. Raman spectra for these films are shown in Fig. 8. These data indicate: (i) that the fraction of microcrystallinity, estimated from the ratio of the scattering at 475 and 520 cm<sup>-1</sup> is lower in the Si–C alloy material than in a material with no carbon added; and (ii) that adding B<sub>2</sub>H<sub>6</sub> further reduces the fraction of microcrystallinity, *i.e.* a film grown from a source gas mixture that includes 0.1% B<sub>2</sub>H<sub>6</sub> shows evidence for microcrystallinity,



Fig. 8. Raman scattering for (a) undoped and (b) doped a-Si–C:H and  $\mu$ c-Si–C films.

whereas a film grown from 1% B<sub>2</sub>H<sub>6</sub> shows no evidence in the Raman spectrum for a detectable microcrystalline component. Table 1 includes conductivity data for these samples grown with hydrogen added downstream, where we note that the films deposited with  $1\% B_2H_6$  have very similar properties independent of whether the film is amorphous or microcrystalline. The effect of adding hydrogen to the downstream mixture is to reduce the band gap, to increase the dark conductivity activation energy and to reduce the dark conductivity. In this instance the changes in activation and conductivity cannot be accounted for with the same value of the conductivity prefactor. Finally, Fig. 9 indicates IR data for several of the same series of films described in Table 1. The main points to focus on are: (i) the spectral region of the SiH stretching vibration,  $2000-2100 \text{ cm}^{-1}$ ; and (ii) the relative strength of the CH<sub>3</sub> features in the spectral range between 1200 and 1500 cm<sup>-1</sup>. We note first that in the two samples grown with hydrogen injected downstream, there are nearly equal IR absorption strengths at about 2000  $\text{cm}^{-1}$  and about  $2075 \text{ cm}^{-1}$ ; these are associated respectively with SiH vibrations at 2000  $cm^{-1}$ , in which the SiH group has only silicon neighbors, and with SiH groups, at 2075  $cm^{-1}$ , where there are one or more carbon atoms back bonded to the SiH group. For the three samples grown without hydrogen dilution, the 2075  $cm^{-1}$  mode dominates. In addition, the three samples grown without hydrogen dilution show stronger features associated with the  $CH_3$  groups. This means: (i) that hydrogen dilution influences the local bonding environments of SiH groups, and that this is independent of the microcrystalline or amorphous nature of the film; and (ii) that addition of hydrogen also effects the concentration of methyl groups. Clearly additional



Fig. 9. IR transmission spectra for (a) a-Si-C:H and (b)  $\mu$ c-Si-C films.

# 5. Applications of $\mu$ c-Si and $\mu$ c-Si–C in device structures

We used these films as the i layers in p-i-n junctions that are fabricated from  $\mu$ c-Si throughout. These p-i-n structures have the following layer dimensions: the p layer and n-layers are 300 Å thick, and the i layer is 2800 Å thick. The p-i-n diodes exhibit rectification ratios of about 10<sup>4</sup> at a 0.5 V bias level and have short circuit current densities of about 4 mA cm<sup>-2</sup>, and open circuit voltages of 0.4 V, in "non-optimized" PV devices, *i.e.* devices with poor contact geometries, and illuminated through absorbing  $\mu$ c-Si p layers that were deposited onto indium tin oxide (ITO).

We also fabricated p-i-n structures with  $\mu$ c-Si-C p layers grown from 0.1% B<sub>2</sub>H<sub>6</sub> source gas mixtures, using x = 0.67. These structures employed heavily doped  $\mu$ c-Si n layers, but had a-Si:H i layers. The n- and p-layer thicknesses were 150 Å and 300 Å respectively, and the i-layer thicknesses were 3000 Å and 4000 Å. The structures were deposited onto ITO substrates and illuminated through the p regions. Open circuit voltages were 0.6 eV, and the short circuit current density under approximately 0.5 AM 1 illumination (50 mW cm<sup>-2</sup> from quartz halogen lamp) were 5.2 mA cm<sup>-2</sup> and 8.1 mA cm<sup>-2</sup> respectively for the 3000 and 4000 Å i layers.

# 6. Summary

We have shown that  $\mu$ c-Si films can be deposited by remote PECVD onto a number of different substrate materials. By introducing the hydrogen dilution downstream, the deposited  $\mu$ c-Si films show no detectable "transition" amorphous layer between substrate materials and deposited  $\mu$ c-Si films. We have also shown that conductivities of  $\mu$ c-Si films can be changed by remotely exciting B<sub>2</sub>H<sub>6</sub>-SiH<sub>4</sub> or PH<sub>3</sub>-SiH<sub>4</sub> mixtures. The highest values of dark conductivity, and the lowest values of the dark conductivity activation energies were comparable to what has been achieved in the conventional GD process. In addition we have identified new and interesting properties in an "intrinsic"  $\mu$ c-Si thin film material. The conductivity of this "intrinsic"  $\mu$ c-Si material, coupled with its photoconductivity and spectral response suggest that it may be used in device applications, including solar cells that are constructed with only  $\mu$ c-Si layers. We have grown intrinsic and doped microcrystalline silicon-carbon alloys, and have performed preliminary measurements of optical, electrical, vibrational and doping properties.

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