
Vol. 515 No. 19
16 July 2007
ISSN 0040-6090
ELSEVIER
thin solid films
International Journal on the Science and Technology of Condensed Matter Films
Proceedings of Symposium I on Thin Films for Large Area Electronics
EMRS 2007 Conference, Nice, France
Proceedings Editor
P. Roca i Cabarrocas
Available online at
ScienceDirect
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Thin Solid Films 515 (2007) 7490 – 7494
www.elsevier.com/locate/tsf

The effect of argon dilution on deposition of microcrystalline silicon by microwave plasma enhanced chemical vapor deposition

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Abstract

Microwave plasma-enhanced chemical vapor deposition (PECVD) is a very promising method for industrial scale fabrication of microcrystalline silicon solar cells since the technique is well applicable for large areas, and high deposition rates can be obtained. We have investigated the effect of Ar dilution on the growth process and the material properties of microcrystalline silicon. The major benefit of Ar addition in the MWPECVD process, using H_2 and SiH_4 as reactant gases, is an improved stabilization of the plasma, in particular at low pressure and MW power. We show, however, that material properties of the microcrystalline silicon layers deteriorate if we partly substitute H_2 by Ar during the deposition. The density of the layers – as expressed by the refractive index – decreases, and the defect density (measured by Fourier transform photocurrent spectroscopy) increases with increasing Ar flow. Investigation of the plasma by optical emission study shows that Ar atoms play a very active role in the dissociation processes of H_2 and SiH_4. Substitution of H_2 by Ar decreases the SiH* emission and increases the Si* emission. On the other hand, the H_α/H_β ratio increases upon substitution of H_2 by Ar. The latter effect shows that Ar addition does not lead to higher electron temperatures and we conclude that the changes of SiH* and Si* emissions are due to dissociation of SiH_4 by Ar* (quenching reactions). The precise role of Ar in MWPECVD of microcrystalline silicon needs further investigation, but we conclude that the usage of this gas should be minimized in order to maximize the quality of the silicon layers.

Keywords: Plasma processing deposition; Silicon; Optical properties; Raman scattering

1. Introduction

Thin-film crystalline silicon solar cells have a great potential for the realization of low-cost/high-efficiency solar cells. So-called 'micromorph' silicon solar cells [1], consisting of a tandem structure of amorphous and microcrystalline silicon, have shown high efficiencies up to 14.7% on a laboratory scale [2]. Due to the relatively large thickness of the microcrystalline absorber layer around 1–2 μm, a high deposition rate for this layer with uniform layer properties on large area is essential for cost effective mass production. So far, the best solar cell results have been obtained by Very High Frequency Plasma Enhanced Chemical Vapor Deposition (VHF-PECVD) [3,4] and Radio Frequency (RF) PECVD [2,5] in the high power, high-pressure depletion regime. Alternative deposition methods that are investigated are, e.g., Hot-Wire CVD [6] and Expanding Thermal Plasma CVD [7].

We present here results on intrinsic microcrystalline silicon layers deposited by microwave PECVD, making use of a linear plasma source in combination with a moving substrate. This method allows a very high uniformity, both in direction of the source, and in direction of the substrate transport. This technique has been developed and successfully transferred to industry for large-area and high-rate deposition of silicon nitride layers applied for anti-reflection, surface and bulk passivation of crystalline silicon solar cells [8].

Research on the application of this microwave technique for the deposition of microcrystalline silicon has started recently, demonstrating the potential of high deposition rates [9–12].

In this paper we investigate the effect of Ar dilution on the deposition process of μc-Si by MWPECVD. Argon helps to stabilize the microwave plasma, in particular at high H_2/SiH_4 ratios and at low power conditions. In the past, some research has been carried out to investigate the effect of Ar dilution on deposition of amorphous and microcrystalline silicon by RF PECVD [13–16]. Although it was found that in some cases the deposition rate could be enhanced by adding Ar, the usage of Ar

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doi:10.1016/j.tsf.2006.11.156

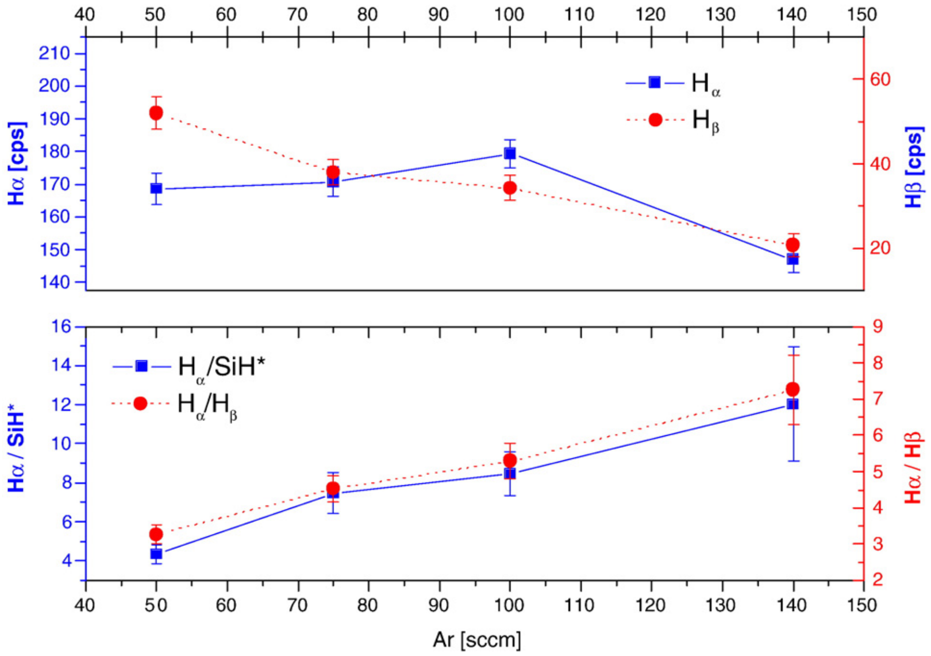

Fig. 1. Optical Emission Spectroscopy data H_α, H_β and SiH emission, for various Ar flows. (Note that the total flow of $Ar+H_2$ was kept constant).

dilution in film silicon deposition by PECVD has not become widespread, and this is merely due to negative effects of this type of dilutant: reduced layer quality due to Ar ion bombardment and enhanced formation of SiH_2 and SiH radicals in the plasma [13,16].

We had two reasons to investigate the effect of Ar dilution on film Si deposition with our MWPECVD system. The first reason is the fact that addition of argon helps to stabilize the plasma, in particular for low microwave power and for high H_2/SiH_4 ratios. The second reason is that, in our roll-to-roll PECVD system, the transfer sluices between the subsequent chambers are purged with argon to minimize cross contamination from chamber to chamber, leading to a very small but detectable concentration of Ar in the deposition chambers.

2. Experimental details

Undoped microcrystalline silicon films have been deposited simultaneously on crystalline silicon wafers and on aluminosilicate glass (Corning 1737) in a single chamber microwave (MW) PECVD reactor, in which a substrate holder with a substrate area of 60×15 cm^2 moves underneath a linear microwave source [10]. We applied a net microwave power of 200 W (i.e. 20% of the maximum power). A mixture of H_2 and Ar is injected in the vicinity of the microwave source, while silane (SiH_4) diluted in H_2 is injected closer to the substrate [10]. In the present study, the silane fraction, defined as SiH_4 flow divided by the total of SiH_4, H_2, and Ar flows ($\Phi_{SiH_4}/(\Phi_{SiH_4}+\Phi_{H_2}+\Phi_{Ar})$), was kept constant at 2.3%. The total flow of diluting gases $Ar+H_2$ was kept at 350 sccm, and we varied the fraction of Ar in the diluting gases. The lowest Ar flow we could apply at this microwave power was 50 sccm. For lower Ar flows the MW plasma is unstable and even extinguishes at this power level. The temperature of the substrates was 300 °C and the pressure during deposition was 0.3 mbar. Under these conditions (with an Ar flow of 50 sccm, but with SiH_4 fraction of 10%) we were able to grow amorphous silicon layers with excellent quality: Urbach tail energy less than 40 meV and $\sigma_{photo}/\sigma_{dark}>1.5\times10^5$. Deposition times were chosen such that layer thicknesses of approximately 1 μm were obtained.

Optical Emission Spectroscopy (OES) in the wavelength range from 200 to 1000 nm has been performed during deposition and the characteristic lines for H_α, H_β and SiH* in the plasma, at 656, 486 and 412 nm, respectively, have been analyzed.

We used Raman spectroscopy (with an Ar laser at 514 nm) to determine the crystallinity of the silicon layers. The Raman spectrum between 300 cm^{-1} and 600 cm^{-1} was deconvoluted into 5 Gaussian peaks: the LA and LO peaks at 330 and 440 cm^{-1}, the amorphous TO peak at 480 cm^{-1}, and two crystalline TO peaks at 505 and at 520 cm^{-1}. The crystalline fraction was calculated as $(I_{520}+I_{505})/(I_{520}+I_{505}+I_{480})$.

From FTIR measurements between 400 cm^{-1} and 4000 cm^{-1}, performed with a Perkin Elmer BX II spectrometer, information on the hydrogen bonding as well as hydrogen concentration of the deposited films have been obtained. The layer thickness and the refractive index at 0.5 eV have been determined by fitting the interference fringes in the IR transmission spectra [10].

The absorption of the silicon layers in the near-infrared has been investigated by Fourier transform photocurrent spectroscopy (FTPS) [17]. To scale the absorption obtained by FTPS, we measured the absorption from 300–1200 nm by reflection and transmission measurements. A single-beam spectrophotometer equipped with an integrating sphere was applied, in order to exclude errors due to optical scattering of porous or rough layers.

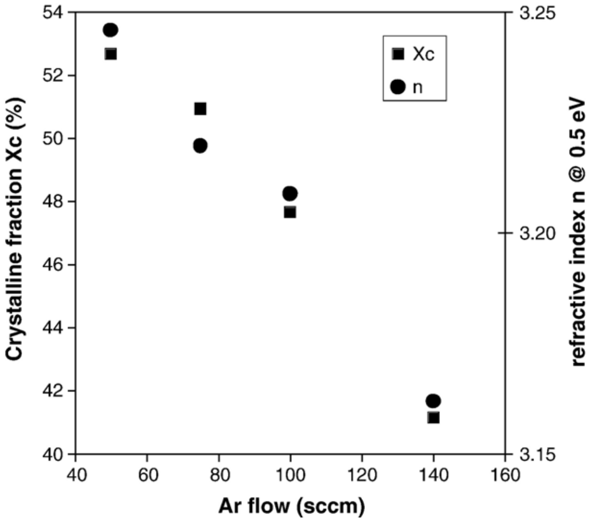

Fig. 2. Crystalline fractions (obtained by Raman spectroscopy) and refractive indices (obtained by FTIR spectroscopy) of silicon layers grown with various Ar flows.

The dark conductivity σ_d has been measured in a 2-point configuration with a source-measure unit (Keithley) after applying Al electrodes on the layers. The photoconductivity σ_{ph} has been measured under simulated AM 1.5 light.

The X-ray diffraction (XRD) measurements have been performed on a Bruker AXS (type D8 Advance). In order to improve the signal to noise ratio of the measurements a grazing incidence setup has been used with a fixed source angle of less than 3°. The diffractogram signals at $2Q=28.4°$ and $2Q=47.3°$, which are assigned to the (111)-plane and (220)-plane of faced-centered cubic silicon, respectively [Ref. [18]], are fitted with Pearson IV functions to analyze changes in the width and area ratio of these two peaks.

3. Results

Optical Emission Spectroscopy reveals interesting phenomena occurring in the plasma when we replace hydrogen by argon in the deposition of microcrystalline silicon. One would expect that both the H_α signal and the H_β signal would decrease if we partially replace H_2 by Ar, but it appears that the intensity of H_β drops more than the intensity of H_α (see Fig. 1), indicating that the average electron temperature T_e decreases if we replace H_2 by Ar.

Further, we observe that the ratio H_α/SiH* increases if we increase the Ar fraction in the diluting gases. It is generally assumed that the ratio H_α/SiH* in the plasma is an important factor determining the crystallinity of the layers, and one would expect larger crystalline fractions for larger Ar fractions.

Analysis of the Raman spectra of the layers, however, shows that the layers become more amorphous, for larger Ar fractions during deposition (see Fig. 2). This implies that the ratio H_α/SiH* in the optical emission is not a satisfactory control parameter for the crystallinity of the layers. The decrease in crystallinity is accompanied with a decrease of the refractive index. This is another surprising result since (micro)crystalline silicon has a lower refractive index than amorphous silicon. This probably indicates that the layers include more (micro)voids when grown with larger amounts of argon.

We did not observe any significant effect of argon on the growth rate of the layers (which was about 0.11 nm/s in these experiments).

The average grain size in the layers decreases if the argon content is increased, based on the widths of the XRD lines. For Ar flow rates of 50, 100 and 140 sccm, the line widths of the (111) peak were respectively 0.53, 0.68 and 0.63° and that of the (220) peak were respectively 0.57, 0.70 and 0.72°. The orientation of the grains is more sensitive to the argon fraction. As can

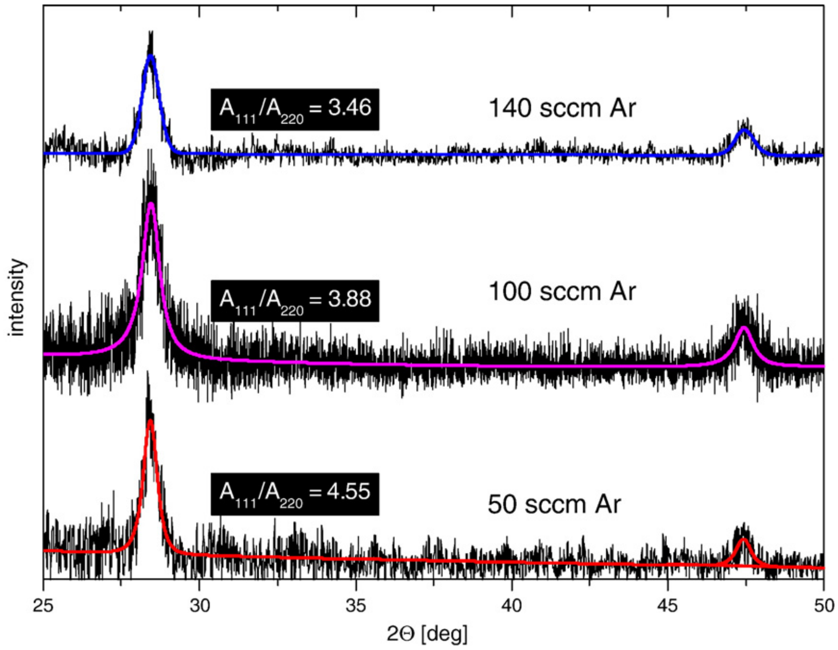

Fig. 3. XRD spectra of three microcrystalline silicon layers grown with Ar flows of respectively 50, 100 and 140 sccm.

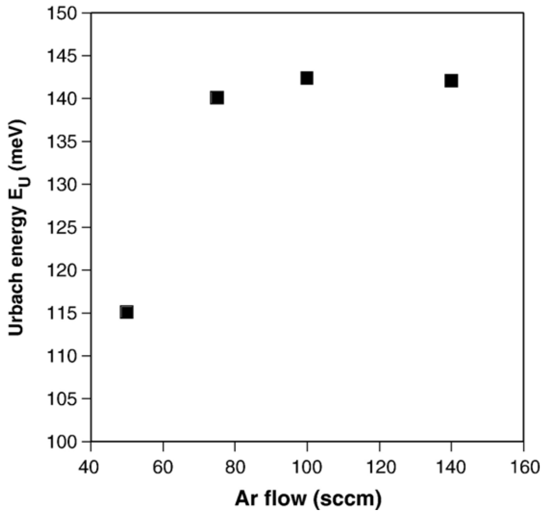

Fig. 4. Urbach tail energy as obtained by FTPS, of silicon layers grown with various Ar flows.

be observed in Fig. 3, the ratio of the (111) over the (220) peak is 4.55, 3.88 and 3.46 for Ar flows of respectively 50, 100 and 140 sccm. This implies that the structure of the layers transforms from a strongly preferentially (111) orientated structure into a more randomly orientated grain structure if hydrogen is replaced by argon as dilutant gas.

The electronic properties of the layers did not improve by increasing the Ar fraction. The Urbach tail energy, determined by the slope of the optical absorption (FTPS) curve below 1.1 eV, shows a significant increase for larger Ar flows (see Fig. 4), indicating larger defect densities. Photo and dark conductivities were not affected by replacement of H_2 by Ar. As shown in Fig. 5, σ_{dark} is about 1×10^{-6} S/cm for all layers and the σ_{photo} is about 2×10^{-5} S/cm, leading to a ratio $\sigma_{\text{photo}}/\sigma_{\text{dark}}$ in the range of 20 for all layers.

The nature of the dark conductivity nonetheless changes upon hydrogen replacement by argon. Although the crystalline fraction in the layers does not change drastically (see Fig. 1), the activation energy for dark conductivity E_a, increases from 0.65 eV to 0.9 eV, and the pre-factor σ_{00} increases from 10^6 to 10^9 S/cm if the argon flow is increased from 50 sccm to 140 sccm (Fig. 6). The increase of E_a suggests that the conductivity becomes more dominated by the amorphous tissue in the layers. Since the amorphous fraction itself does not change significantly, we assume that the change in E_a results from change in crystallinity grading and/or from change in grain orientation in the layers.

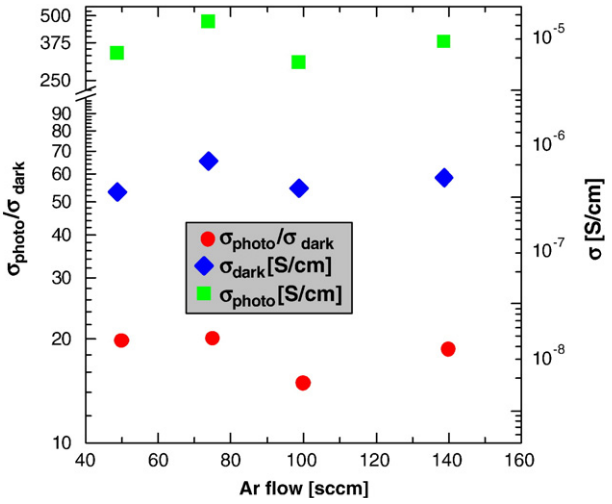

Fig. 5. Photo and dark conductivities of μc-Si layers grown with various Ar flows.

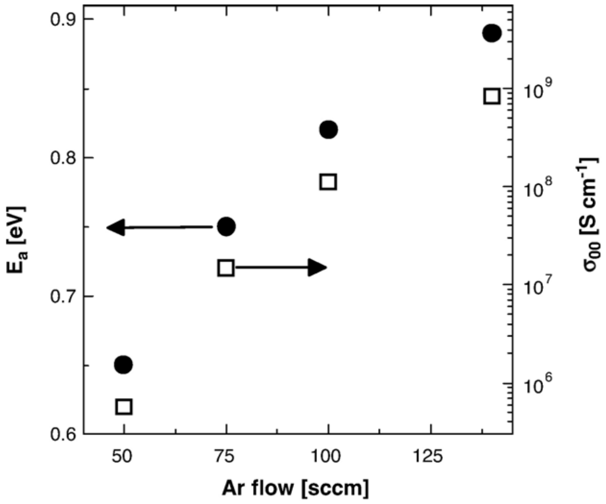

Fig. 6. Activation energy E_a and pre-factor σ_{00} of σ_{dark}, measured in the temperature range between 30 and 120 °C.

4. Discussion

Argon is not an inert gas in a H_2–SiH_4 plasma. The metastable Ar* radicals which are formed in the plasma play an active role in both the dissociation of SiH_4 and of H_2. According to Kushner [13] the following reactions will occur (in an RF plasma):

$$SiH_4 + Ar^{*} \rightarrow SiH_3 + H + Ar\,(k = 1.4\times10^{-10}\text{cm}^{-3}\text{s}^{-1})$$

$$SiH_4 + Ar^{*} \rightarrow SiH_2 + 2H + Ar\,(k = 2.6\times10^{-10}\text{cm}^{-3}\text{s}^{-1})$$

$$H_2 + Ar^{*} \rightarrow 2H + Ar\,(k = 7\times10^{-11}\text{cm}^{-3}\text{s}^{-1})$$

The rate constants clearly indicate that the Ar* metastables favor the formation of SiH_2 species, in contrast to SiH_4 dissociation by electron impact, where the ratio of SiH_2 over SiH_3 formation is about 1:8. This enhanced formation of SiH_2 species, at the expense of SiH_3 formation, can explain the observed increase in amorphous fraction and void density. It is well known that the surface reaction probability of SiH_2 is much higher than that of SiH_3 [19], and that this higher sticking probability generally leads to less dense silicon networks.

The observed increase of H_α/H_β ratio in OES points at a reduction of the average electron temperature T_e for larger Ar fractions. The lower T_e is probably a consequence of a higher electron density n_e, such that the average energy transfer from the EM field per electron becomes smaller in a plasma with a higher Ar fraction. The electron density in an Ar plasma is larger than in a H_2 plasma because the rate of electron–ion recombination reaction ($e+\mathrm{Ar}^+\rightarrow\mathrm{Ar}^*$; respectively $e+\mathrm{H}_2^+\rightarrow\mathrm{H}^*+\mathrm{H}$) is about 6 orders of magnitude smaller for Ar than for H_2, while the ionization rates of both species are about the same [13].

A second mechanism – next to plasma chemistry – through which argon might affect the structure of the deposited silicon layers, is ion bombardment. This mechanism, however, is far less important in a microwave driven plasma than in a radio-frequency plasma. Due to the high frequency (2.45 GHz), ion energies at the microwave plasma conditions we use are typically in the order of 1 eV where in RF plasmas' ion energies are typically in the range of 20–100 eV.

So we conclude that the main effect of argon dilution to the growth of silicon layers in MWPECVD is due to the change in plasma chemistry, but more detailed plasma diagnostics are required to validate these hypotheses.

5. Conclusions

Addition of argon to a H_2/SiH_4 plasma can help to stabilize the plasma in microwave PECVD, in particular at low microwave power and high silane dilution ratios, but it has a detrimental effect on the density of the layers. We did not observe any significant effect of argon on the growth rate of the layers. The structure of the layers becomes more amorphous and the layers contain more defects when H_2 is partially replaced by Ar as process gas. The main effect of argon dilution to the growth of silicon layers in MWPECVD is probably due to a change in plasma chemistry, where Ar* metastables favor the formation of (unwanted) SiH_2 species at the expense of SiH_3 formation.

Acknowledgements

This work has been financially supported by the Dutch Ministry of Economic Affairs (Project No. TSIN3043) and by the European Commission under contract no. INCO-CT-2004-509178.

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