Comparative Study of Low-temperature PECVD of Amorphous Silicon using Mono-, Di-, Trisilane and Cyclohexasilane

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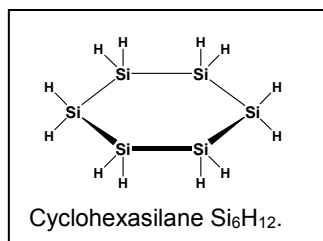North Dakota State University, Fargo, ND 58108 USA

ABSTRACT

The hydrogenated amorphous silicon a-Si:H films were grown by plasma-enhanced chemical vapor deposition (PECVD) using liquid cyclohexasilane Si_6H_{12} (CHS). The growth rate of a-Si:H was studied as a function of substrate temperatures in the range of 30 ^oC<T<450 ^oC using deposition conditions that were optimized for monosilane SiH_4. The same parameters were used for a-Si:H films grown using disilane (Si_2H_6) and trisilane (Si_3H_8) precursors. It was found that the a-Si:H film growth rate for CHS is lower with respect to those for mono-, di- and trisilane in an Ar plasma. Addition of ~10% of H_2 dramatically increases the deposition rate for CHS-based films to __ nm/min – a 700% increase. The as-deposited films were characterized by FTIR and Raman spectroscopy to probe the hydrogen content and local bonding environment. It was found that the films grown using Ar/H_2 mixtures as carrier gas have a reduced hydrogen content relative to polysilane fragments indicating higher quality amorphous silicon.

INTRODUCTION

The development of lower-temperature PECVD routes to silicon-based electronic materials is of interest given the promise of producing flexible solar cells on cost-effective substrates such as polyethylene terephthalate. In addition, the demonstration of higher-growth rates for PECVD silicon films may address a bottleneck in some existing photovoltaic manufacturing technologies. It was recently reported that the use of neopentasilane (Si_5H_{12}) as a CVD precursor leads to significantly higher growth rates for epitaxial silicon as compared to lower-order silanes such as silane (SiH_4) and disilane (Si_2H_6).[1]

Recently a synthetic route to a higher-order silane precursor in the form of cyclohexasilane, Si_6H_{12} or CHS was developed.[2] We have recently initiated a study investigating the use of CHS as a precursor in the PECVD growth of amorphous and polycrystalline silicon thin films. In order to establish the value of CHS as a CVD precursor, silicon films were also grown from SiH_4, Si_2H_6 and trisilane (Si_3H_8) under identical conditions. In this work we report the amorphous hydrogenated silicon a-Si:H growth rate dependence upon the deposition temperature,

Cyclohexasilane Si_6H_{12}.

pressure and plasma power. The films were characterized by FTIR and Raman spectroscopy.

EXPERIMENTAL

The a-Si:H films were deposited on glass or HF-treated Si (100) substrates by PECVD. The 4% mono-, di- and trisilane in He were used as precursors with 25 sccm flow rate. The CHS was utilized as the liquid precursor source with a home-made bubbler and custom lines for delivery into an Oxford 100 Plus PECVD reactor (13.56 MHz). Up to 25 sccm of Ar or H_2 were used as the carrier gas. For the monosilane SiH_4 precursor a maximum a-Si:H deposition rate of 2.56 A/sec was achieved at a plasma power of .094 watts/cm^2 when the reactor pressure was set to 1 Torr with 140 sccm of Ar added to the process. For the sake of comparison, the same deposition conditions were used for disilane, trisilane and CHS. The substrate platen temperature was varied from 30 to 450 ^oC with a growth time of 15 min for all samples. Film thicknesses were determined using ellipsometry. Bruker Vertex 70 FTIR spectrometer with a range from 400 to 4000 cm^{-1}, equipped with Harrick Scientific Products, Inc GATR™ grazing angle ATR accessory, was used to analyze the hydrogen content and its bonding environments. The Raman spectra were collected using HORIBA Jobin Yvon Inc. LabRAM ARAMIS confocal Raman microscope with 532 nm laser excitation. The hydrogen content was determined from the integral intensity of the absorption peaks at 2000-2200 cm^{-1} which includes stretching vibrations of Si-H bonds in every possible bond configurations. A relationship between hydrogen concentration in cm^{-3} (N_H) and the absorption coefficient (α) was presented by Brodsky, Cardona and Cuomo (BCC).[3]

$$N_H(atom\%) = A \times \frac{1}{d_{Si}} \int (\alpha/\omega)d\omega; \qquad (1)$$

where A is a proportionality constant that is band dependent; the result can be expressed in atomic % by normalizing it to the atomic density of the crystalline silicon d_{Si} = 5×10^{22} cm^{-3} (Eq. 1). For the ν(Si-H) stretching modes[4] we used A = 1.1×10^{20} cm^{-2}.

RESULTS AND DISCUSSION

The deposition rate versus substrate temperature is shown in Figure 1. The deposition rate increases about 20% when SiH_4 was substituted with Si_2H_6, and practically does not change for the higher order trisilane Si_3H_8.
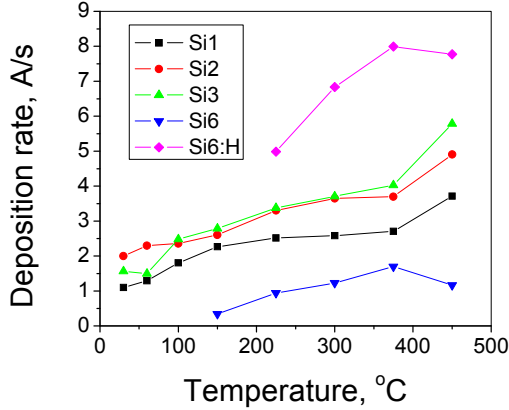
Figure 1. PECVD a-Si deposition rates for SiH_4 (--), Si_2H_6 (--), Si_3H_8 (--), Si_6H_{12} (--) and Si_6H_{12}:H (--) precursors.

The deposition rate for CHS under identical PECVD conditions is about 4 times lower. However, addition of ~10% (by volume) of hydrogen (Si_6H_{12}:H) into the Ar plasma allows improving the deposition rate almost by 700% (at 375 °C)! The relative low deposition rates for the gaseous silanes as well as CHS suggest that in these deposition conditions the major fraction of plasma-induced radicals reaching the surface is not incorporated,[5] but recombines to higher silanes. The low sticking coefficient and relative high surface mobility may contribute to the formation of well-configured amorphous silicon network. In contrast, the substantial increase of the deposition rate with a moderate hydrogen dilution may imply the higher sticking coefficient facilitated by high hydrogen concentration on the surface, and thus formation of pronounced polysilane microstructure. To analyze the short range structure of the deposited materials, the materials were characterized by FTIR and Raman spectroscopies in the ν(Si-H) stretching and silicon TO modes frequency range, respectively.

For PECVD materials it is known that hydrogen content below ~8 at.% generally leads to a high density of defects while hydrogen content above ~12 at.% leads to dihydride bond (SiH_2) formation and inclusion of polysilane clusters. The hydrogen content in the a-Si:H films prepared in this study is shown in Figure 2 as a function of substrate temperature.

When only Ar plasma is used for deposition, the hydrogen concentration increases with increased substrate temperature reaching a maximum around 200 °C and then dropping gradually with further substrate temperature increase for all studied silanes. The hydrogen concentration in maximum is increasing with the increase of the precursor molecular weight suggesting that substantial amount of poly-silane –(SiH_2)$_n$– fragments is present. In contrast, in Ar/H$_2$ plasma the film hydrogen content is practically temperature independent in the 225<T<450 °C deposition temperature range.
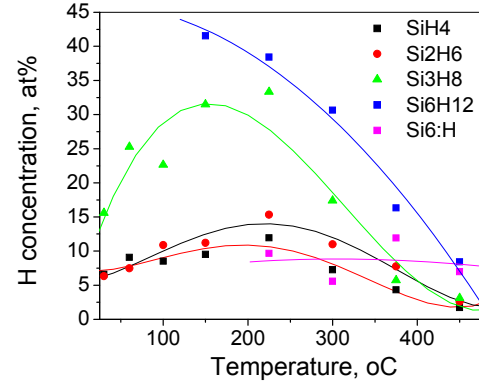

Figure 2. The hydrogen content in PECVD a-Si films on glass for SiH_4 (-), Si_2H_6 (-), Si_3H_8 (--), Si_6H_{12} (-) and Si_6H_{12} :H (-) precursors. Lines represent a polynomial fit.

To evaluate the local bonding environment it is often useful to introduce a "microcrystalline parameter" R*, as a figure of merit indicating the fraction of atoms that are not in isolated SiH bonds surrounded by a dense silicon network (ν(SiH) = 2000 cm^{-1}). Hydrogen bonded in different fashions representing monohydride bonds at a "free" surface, e.g. a void, isolated dihydride SiH_2 bonds, cluster SiH or polysilane –(SiH_2)$_n$– fragments, have ν(SiH) shifted 60 - 100 cm^{-1} to higher wavenumbers.[3] The parameter R* thus is defined as[6]

$$R^* = \frac{N_{2100}}{N_{2100} + N_{2000}};$$

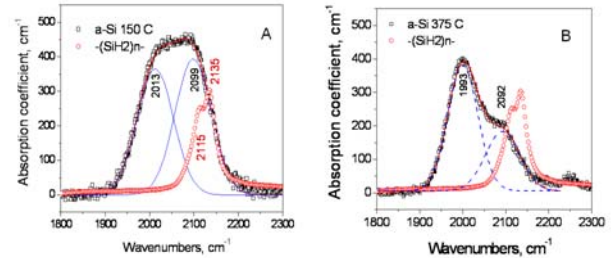Ideally, the R* value should be zero, but for the practical purposes R* < 0.1 is acceptable.

Figure 3. The ν(Si-H) stretching modes in IR spectra of the a-Si:H films deposited at 150 (A) and 375 °C (B) using Si_2H_6 precursor. The spectrum of polysilane (red) is shown for comparison.

The ν(Si-H) stretching modes of the a-Si:H films deposited at 150 and 375 °C using Si_2H_6 as well as polysilane are shown in Figures 3A and 3B. The comparison of the shapes and positions of these modes with those of polysilane suggests that the films contain hydrogen as isolated SiH as well as clustered SiH and SiH_2 since both characteristic peaks at ~2000 cm^{-1} and ~2100 cm^{-1} can be deconvoluted from the broad envelope (blue lines in Figure 3).
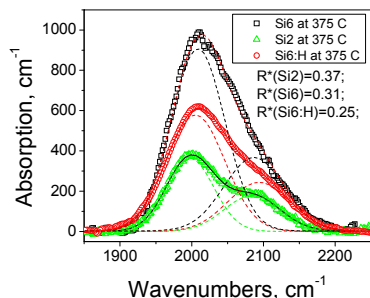
Figure 4. The ν(Si-H) stretching modes in IR spectra of the a-Si:H films deposited at 375 ^{o}C using Si_2H_6 (black), Si_6H_{12} (red) and Si_6H_{12}:H (green) precursors. Lines represent a two Gaussian fit.

The calculated R* factor is decreasing from 0.51 at 150 ^{o}C to 0.35 at 375 ^{o}C implying that the concentration of the SiH bonded hydrogens increases at the expense of SiH_2 ones with the increase of the substrate temperature. Similar behavior was observed for all studied silanes. Nevertheless, the deposited materials remain very disordered even at 450 ^{o}C since the R* factor values remain above 0.3.

In contrast, when Ar/H_2 plasma was used, the hydrogen concentration at the level of 7±1 at% and the R* factor of 0.25±0.5 do not change with the increase of the substrate temperatures (Fig. 4) suggesting that the hydrogen addition stabilizes the short range order of the amorphous hydrogenated silicon deposited using CHS as a precursor. However, the achievement of electronic-grade materials shall require further process optimization.
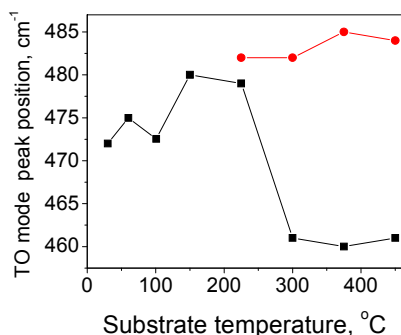

Figure 5. The TO mode peak position vs. the substrate temperature of the films grown using Si_2H_6 (black) and Si_6H_{12}:H precursor (red).

The position of the Raman active transverse optical (TO) mode is also very sensitive to the degree of disorder in the silicon network. The Raman spectrum of single crystal Si shows a sharp TO mode associated peak at 521 cm^{-1}, whereas the amorphous Si signal appears as a much broader feature at 480-500 cm^{-1}. In our study the maxima of the TO modes are shifted toward higher wavenumbers as the higher hydrogen content (and local order) in the films increases with increasing the substrate temperature

from 30 to ~225 ^{o}C, Figure 5 (black). When the substrate temperature is increased further, the hydrogen content drops as does the TO peak frequencies. In contrast, frequencies of the silicon TO modes of the a-Si:H films deposited using CHS in Ar/H_2 plasma are temperature independent for the whole studied temperature range suggesting less disordered material.

CONCLUSION

1. The route toward PECVD deposition of the electronic quality hydrogenated amorphous silicon films using CHS precursor have been identified.
2. The a-Si:H film growth rate for CHS is lower with respect to those for mono-, di- and trisilane in an Ar plasma.
3. Addition of ~10% of H_2 dramatically increases the deposition rate (~700%). The obtained films have much lower content of hydrogen relative to polysilane fragments indicative of higher quality amorphous silicon.

ACKNOWLEDGMENTS

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