Hydrogen content of plasma deposited a-Si:H

HYDROGEN CONTENT OF PLASMA DEPOSITED a-Si:H

R.J. Severens, G.J.H. Brussaard, H.J.M. Verhoeven, M.C.M. van de Sanden and D.C. Schram
Eindoven University of Technology, - Department of Physics - P.O. Box 513 - 5600 MB Eindhoven, The Netherlands
Tel: (+31) 40 474369 - Fax: (+31) 40 456442

Amorphous hydrogenated silicon is deposited using a remote argon/hydrogen plasma. The plasma is generated in a DC thermal arc and expands into a low pressure chamber (20 Pa). Pure silane is injected into the plasma jet immediately after the arc source in a typical flow mixture of Ar:H_2:SiH_4=55:10:6 scc/s. At the low T_e in the jet (0.3 eV);silane radicals are produced mainly by hydrogen abstraction. In-situ ellipsometry yields refractive indices of 3.6-4.2 at 632.8 nm and growth rates of 10-20 nm/s. FTIR analysis yields a hydrogen content of 9-25 at.% and refractive indices of 2.7-3.3 in the infrared. The SiH density decreases with increasing hydrogen content, whereas the SiH_2 density increases, indicating a deterioration of the microstructure. The optical bandgap remains constant at approximately 1.72 eV. The photoconductivity is of the order 10^{-6} $(\Omega cm)^{-1}$ and the photorespons 10^6.

1. Introduction

In recent years the emphasis of amorphous hydrogenated silicon deposition has been on the relation between quality of the deposited layer and characteristics of the growth process as growth rate and radical composition. At the same time approaches have been sought to increase the growth rate while maintaining quality. Several approaches have been followed e.g. by the increase of the frequency of RF excited systems. Values of up to 2 nm/s have been reached; even improved characteristics as lower defect density are sometimes observed [1],[2].

Also the kinetics of the growth process have been addressed supported by kinetic models with increasing complexity. It is generally believed that SiH_3 is the preferred precursor as its sticking coefficient is low permitting sufficiently long dwelling time on the surface for growth of layers of low defect density. Successful experiments with hot wire schemes appear to be in support of this line of thinking. It should be noted though that still a complete picture is lacking and that also other combination of radical composition and ion richer fluences may eventually prove to be possible.

To address these questions and to seek for even higher growth rates a different approach is followed in the present work. A high intensity thermal plasma source produces a Ar/H_2 plasma which expands first supersonically and then subsonically into a low pressure background (0.2 mbar), cf. Fig. 1. The source is a cascaded arc with three cathodes at the upstream and an anode nozzle at the downstream side. At the used carrier gas admixtures Ar/H_2, 55/10 scc/s the chemical energy is expected to be carried by H^+ ions and H. atoms. In the expansion 6 scc/s of SiH_4 flow is injected. At the estimated fluences of 10^{19}/s ions and 5.10^{20}/s atoms the major kinetic chain is expected to be [3]:

$$SiH_4 + H \rightarrow SiH_3 + H_2 \ (\Delta E = -0.5 \text{ eV}) \qquad (1)$$

thus producing the desired precursor radical. Still also the ions may contribute to the radicalization in a sequence of charge excited exchange and dissociative recombination [3]:

$$SiH_4 + H^+ \rightarrow SiH_3^+ + H_2 \ (\Delta E = -5.8 \text{ eV}) \qquad (2)$$

followed by $$SiH_3^+ + e \rightarrow SiH^* + H_2 \text{ or } \rightarrow SiH_2 + H \qquad (3)$$

It is expected that the radical reaction (1) prevails in view of the dominance of the [H] concentration over H^+.

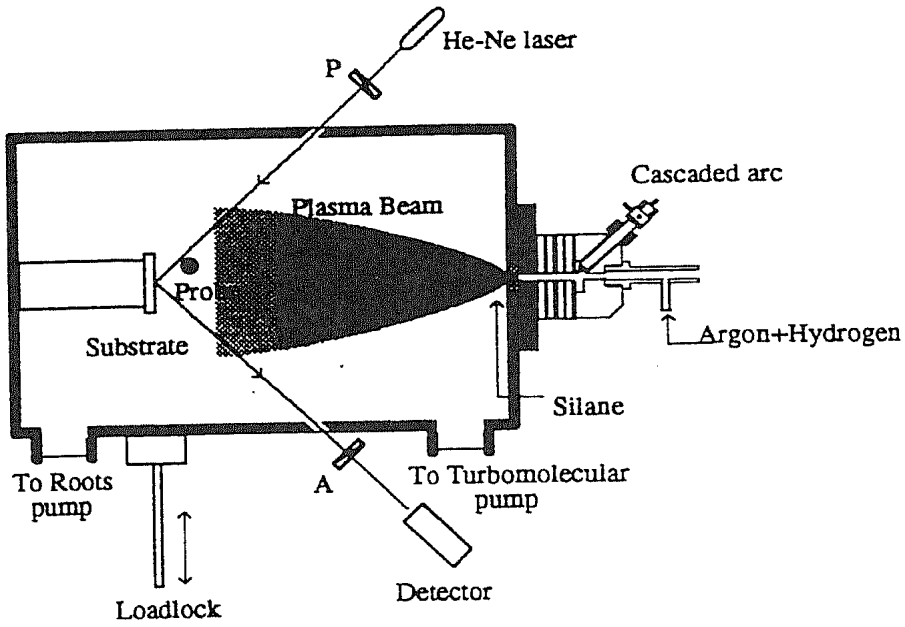

Fig. 1 Expanding plasma beam deposition set-up.

The silane fragments and the transferred chemical energy is carried by the near to sonic flow to the substrate, guaranteeing an efficient radical transport. At the substrate, which is temperature controlled, the SiH_3 radicals contribute to the growing layer, whereas the [H] atoms lead to etching and control the H- content in the growing film.
As the residence time (typically 0.1 sec) is longer than the recirculation time, wall association contributes to the formation of hydrogen molecules [4] which are admixed close to the nozzle with the primary beam. This recirculation flux is estimated to be 10 times higher than the primary [H]-atom flux from the arc source. Hence the admixing of primary [H] beam from the source with the secundary recirculating [H_2] flow leads to a dissociation degree of 10% in the expanding plasma. Whether ro-vibrationally excited molecules contribute also to the chemical kinetics is not known.

2. Results on ion density and growth rate

With electrostatic probes the ion saturation current has been measured close to the substrate. From separate hydrogen experiments it is known that charge exchange and dissociative recombination leads to an efficient recombination of positive ions. Similar processes with silane (cf. eqs. 2 and 3) may lead to Si^+-ions which have a low ionization potential and are

relatively stable. If hence it is assumed that predominantly Si-based ions remain, the probe current can be translated to an ion density. The results are shown in Fig. 2.

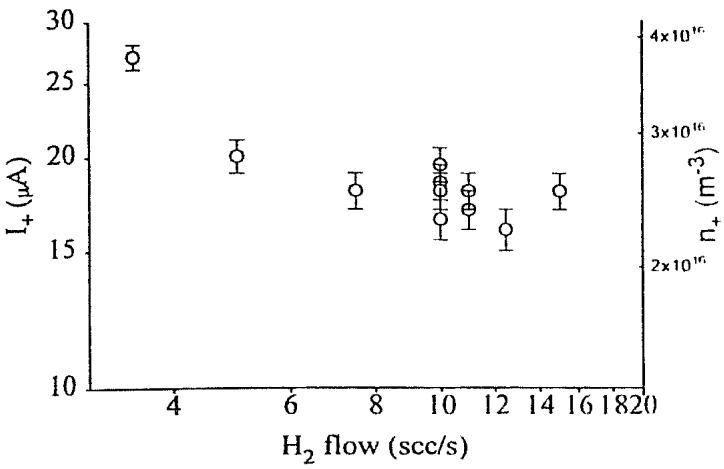

Fig. 2 Langmuir probe ion saturation current and resulting ion density as a function of hydrogen flow.

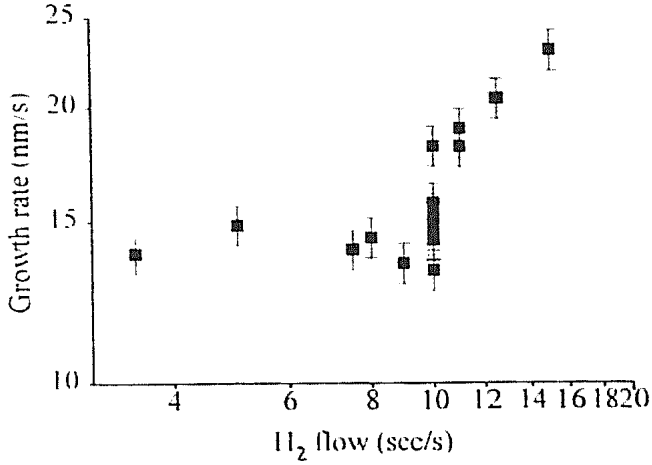

Fig. 3 growth rate vs hydrogen flow

With the estimated flow velocity an ion flux can be estimated which appears to be substantially smaller than the flux which would correspond to the observed growth rate, cf. Fig. 3. Hence it is concluded that ions do not contribute substantially to the growth of the layer. An estimate of the flux of SiH_3 radicals does correspond to the observed growth rate if an deposition efficiency of around 10% is assumed. The increase of growth rate with increasing H_2 flow above 10 scc/s is also an indication for a dominance of radical contribution. One of the possible mechanisms is the creation of more growth-sites by abstraction of H-atoms in the growing layer with H_2 formation.

3. Results on quality of the layer

Several material properties have been measured. Fourier transform infrared absorption experiments (FTIR) of the resulting layers give the SiH and SiH_2 content in the film. From the 640 cm^{-1} wagging mode the hydrogen content is obtained, whereas the 2000 cm^{-1} and 2100 cm^{-1} stretching modes yield the SiH and SiH_2 concentration. With nuclear techniques a second -H- concentration is measured as well as the oxygen concentration.
Material properties are listed in table 1.

n_{HeNe}	4.2	σ_{photo}	$10^{-6}\ \Omega^{-1}\ cm^{-1}$
n_{IR}	3.3	$\sigma_{photo}/\sigma_{dark}$	10^6
[H]	10%	E_{act}	0.8-1 eV
$I_{2100}/(I_{2000}+I_{2100}$	0.2	[O]	<0.3%
FWHM(I_{2000})	110 cm^{-1}	DOS_{midgap}	$3.10^{16}\ cm^{-3}$
$E_{gap,\ Tauc}$	1.7 eV	μτ (300 K)	$10^{-6}\ cm^2V^{-1}$

In Fig. 4 the refractive index is given as a function of the hydrogen content in the film, showing that the highest index of refraction is obtained at the lowest hydrogen content. With increasing H content the SiH_2 contribution increases, whereas the SiH one decreases [3].

From the results obtained it can be concluded that the obtained material approaches the desired material quality. Two aspects need still to be addressed: the too low photoconductivity and the by a factor of 10 too high defect density. Both may be related to the too high SiH_2 fraction in the film. The oxygen concentration is below 0.1% but may still be too high, which would also contribute to the observed discrepancy. In subsequent experiments further optimization of the plasma parameters and substrate conditions will be pursued and aimed at lowering the oxygen content and the SiH_2 mode contribution.

4. Results of D-H isotope experiments

Another information comes from isotopic experiments: injection of D_2 in stead of H_2 in the arc. It should be noted that the D_2-fed arc source is known to be slightly more efficient than the H_2 arc and hence may result in a slightly higher ion flow. However the main difference will be the replacement of H-atoms by D-atoms. The H-atom content in the silane flow is similar to the D-content in the arc flow. As it is assumed that the abstraction reaction is efficient and full recirculation is assumed for hydrogen isotopes it follows that in the vessel wall the H/D ratio must be close to 1.

From experiments it follows however that the D-content in the film is only 10%, cf. Fig. 5. From this result we conclude that recirculation of SiH_nD_m is relatively unimportant in the growth process, as a full recycling model would lead to SiH_2D_2 and 50% H/D ratio in the film. Hence it appears that direct flow deposition is dominant and that D-atoms preferably contribute to abstraction and removal of remaining H-atoms in the growing film.

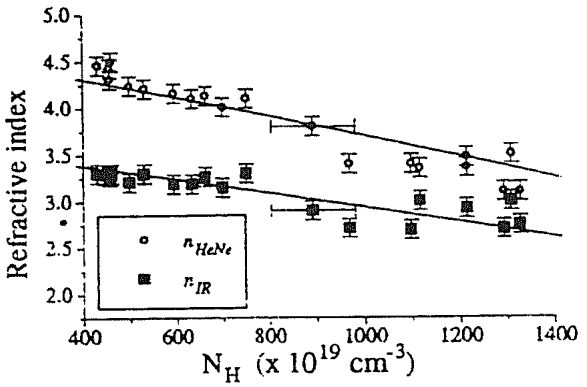

Fig. 4 Refractive index as a function of H content in the film.

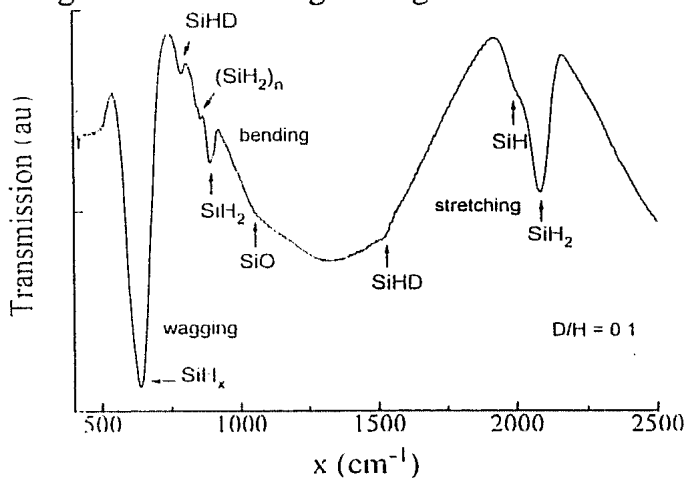

Fig. 5 Example of a FTIR spectrum of material deposited with $SiH_4/D_2/Ar$ plasma.

References

[1] A. Matsuda, Proc. workshop Industrial Applications of Plasma Physics, Varenna, 1992, p 405, publ. Sociètà Italiana di Fisica.

[2] W.G.J.M. van Sark, J. Bezemer, E.M.B. Heller, M. Kars, W.F. van der Weg, 1995 Spring meeting MRS, San Francisco, April 17-21, USA

[3] R.J. Severens et al., 1995 Spring meeting MRS, San Francisco, April 17-21, USA.

[4] M.J. de Graaf et al., Phys. Rev. E, 48, 1993, 2098-2102.

[5] R.F.G. Meulenbroeks, private communication 1994, to be published.

Acknowledgement

This work has been supported by grants of the NOVEM and of the KNAW.