# DEFINED AND REPRODUCIBLE OPTICAL AND ELECTRONIC PROPERTIES OF a-Si:H BY SPECIFIC PLASMA CONDITIONS

G.H. Bauer, G. Bilger
Institut fuer Physikalische Elektronik, Universitaet Stuttgart
Boeblingerstrasse 70, D-7000 Stuttgart-1, F.R.G.

## ABSTRACT

Plasma chemical preparation of a-Si:H films in rf-sputtering and dc-glow discharge has been investigated by plasma diagnostic methods for control of reproducibility of the plasma state and for evaluation of parameters especially for densities of species Si, SiH composing the layer. Film analyses show that properties (absorption, band gap, densities of states) are governed by the plasma state. The correlation of plasma diagnostics and film analyses provides means for an optimization of preparation.

## 1. INTRODUCTION

Electronic and optical properties of amorphous silicon like band gap and absorption coefficient promise a remarkable suitability for photovoltaic applications/1/. Undoped and doped a-Si:H films generally can be prepared by plasma chemical methods in different types of gas discharges under various physical conditions, e.g. by decomposition of silane/2,3,4/, by evaporation of silicon and treatment in hydrogen/5/ or by rf-sputtering in hydrogen/rare gas mixtures/6,7/.
The main requirements for the preparation of films with reproducible properties which have to be enforced are reproducibility and temporal stability of the plasma state. Neglecting these conditions a great lack of reproducibility and comparability of film properties must be expected.

## 2. EXPERIMENTAL SETUP FOR FILM PREPARATION AND PLASMA DIAGNOSTIC

Two high vacuum systems ($\approx 10^{-7}$ mbar) (see figure 1) with quartz windows have been used to prepare a-Si:H films in

either a rf-sputtering plasma (13.5 MHz) in $Ar/H_2$, $Ne/H_2$, and $Kr/H_2$ mixtures with different compositions and ranges of total pressure ($5\times10^{-3}$ - $3\times10^{-2}$ mbar),
or a dc-glow discharge in $SiH_4$ and in mixtures of $SiH_4/Ar$ and $H_2/Ar$ ($10^{-2}$ - $10^{0}$ mbar) with a silicon cathode.

Impurities and composition of the neutral gas are analyzed and controlled by a quadrupole mass spectrometer which can be connected to each discharge chamber by a pressure reduction system. The gas flows are regulated with respect to constant pressure in the system. Layer thickness and deposition rates have been analyzed during preparation process; the power supply for rf- and dc-discharges have been stabilized and duration of processes is regulated by a timing system.

The radiation of each plasma can be focused by a system of parabolic mirrors to the entrance slit of a 0.3m grating monochromator (wavelength resolution 26Å/mm). For a local scan of the radiation one mirror can be moved/rotated by a stepping motor.
To the monochromator output a photomultiplier which is cooled for noise reduction ($-30^{o}C$) has been attached to feed the signal to a lock-in-amplifier.

## 3. PLASMA ANALYSES

In these discharges, each showing a specific set of figures and ranges of plasma parameters, species like Si, SiH are generated by particular mechanisms in the plasma and interactions of the plasma with electrodes:

| | generation of Si | generation of $SiH_x$ |
|---|---|---|
| rf-sputtering | cathode sputtering | reactive interact. of Si and hydrogen |
| dc-glow disch. | cathode sputtering, dissociat. of $SiH_n$ | reactive interact. of Si and hydrogen, dissociat. of $SiH_n$ |

In figure 2 typical emission spectra of the rf-sputtering plasma and the dc-glow discharge indicate atomic lines of silicon (SiI) and rotational bands of electronic transitions ($A^2\Delta - X^2\Pi$) of the SiH molecule. Since the intensities of lines and bands on the one hand depend on the mechanisms of excitation to the upper level and on the kinds and probabilities of transitions to the lower level, on the other hand depend on the densities of the particular species, the densities of Si and SiH can be calculated by a deconvolution of their line intensities with respect to the function of excitation. This function has been evaluated from lines of atomic components of the neutral gas, assuming that the excitation only is effected by electron impact from the ground state or near by.
If there would be a remarkable contribution of excitations of SiH resulting from chemical reactions the kinetic energy (translational and rotational) should reflect this amount within the mean time of collisions ($10^{-6}$ s). As the rotational temperature of SiH which can be evaluated from rotational bands is in the range of the gas temperature, excitations resulting from chemical reactions have not been taken into account. A contribution to the excitation of atomic/ionic lines can be neglected as the electron "temperature" of lines of Si and of the atomic components of the neutral gas correspond very well.
Figure 3 shows the relative densities of Si and SiH generated in rf-sputtering and dc-glow discharge as a function of applied voltage resp. current density. An increase of applied voltage increases the number and as well the energy of charged particles and thus higher sputtering rates at the cathode/8/ resp. higher rates of collisional dissociations of $SiH_x$ are effected. By this an increase of $n_{Si}$ is enforced, whereas the density of SiH can only be weakly increased (rf-sputt.) resp. is decreased (dc-g.d.).

A defined and controlled variation of $n_{Si}$ and $n_{SiH}$ can also be achieved by means of variations of the plasma state when changing applied voltage/current density as demonstrated above. Moreover defined and reproducible variations of densities of those species can be effected by a variation of total pressure which is

reported elsewhere/9,10/.
Figure 4 summarizes the deposition rates for films prepared by rf-sputtering and dc-glow discharge which also reflect the increased generation and the increased density of mainly Si as a function of applied voltage. In the dc-glow discharge an obvious kink in the deposition rate can be observed which is correlated to a remarkable contribution of dc-sputtered silicon.
Figure 5 demonstrates this sputtering effect in a glow discharge in Ar at different pressures and cathode current densities. The density of cathode sputtered material is strongly increased by an increase of voltage and of mean free path of particles.
As a consequence of this components of the cathode (potentially dopants) are transported to the gas phase and are incorporated into the film.

## 4. FILM ANALYSES

The optical and electronic properties of the films have been analyzed by

- SEM methods to prove lateral homogeniety and film thickness,
- spectral transmission (300nm-2000nm) for calculation of normalized absorption coefficients and evaluation of thickness from interference effects,
- temperature dependent electrical conductivity, which shows particular transport mechanisms and their activation energies/11/,
- spectral yield of photoluminescence which is a criterion for low density of states,
- photoconductivity (integral and spectral resolved) yielding an estimation for life times of electrons/12/.

The evaluation of data from these analyses show for films prepared by both methods good reproducibility and lateral homogeniety. Lateral variations of thickness in films with $7x7cm^2$ do not exceed 7%.
In figures 6,7,8 the normalized absorption coefficients, relative yields of photoluminescence and temperature dependent electrical conductivity are shown for films of rf-sputtering and dc-glow discharge.
For both methods of preparation a defined variation of plasma parameters enforcing a defined and reproducible set of densities of species composing the layer obviously effects a shift of edge of absorption, edge and yield of photoluminescence and of room temperature conductivity and its activation energy for extended states conduction which indicates the position of the Fermi level.

## 5. INTERPRETATION

Though little information is known so far about kinetics of surface reactions and deposition mechanisms when an amorphous film is growing, it has been proved that the contents of hydrogen for the saturation of dangling bonds in a-Si:H can be controlled on the one hand by the substrate temperature and at least can be limited by the amount of $H_2$ in the plasma, on the other hand seems to be strongly governed by the densities of plasma generated species that means by the plasma state itself.
These investigations demonstrate that amongst the influence of deposition conditions which is well known/13,14/ and that of the

composition of the neutral gas/10/ the plasma state turns out to be an important variable for the preparation of amorphous silicon films.
A criterion for a qualitative and comparative indication of the density of states can be deduced from the correlation of absorption coefficient, photoluminescence and conductivity. If we regard a simplified function of density of states (see figure 9) for low(1) and high(2) density we can assume that the edge of absorption corresponds to $(E_c-E_v)$, the edge of photoluminescence however as it results from transitiions between band tails/15/ is correlated to $(E_a-E_b)$. Consequently a film with low density of states should show:

1) small energetic distances between edge of absorption and edge of photoluminescence(small$(E_c-E_v)-(E_a-E_b)$),
2) relatively high yield of photoluminescence as there are comparatively low rates of radiationless recombinations to the valence band,
3) sharp edges of optical absorption which means high transmission for photons with energies below gap energy,
4) high room temperature dark resistivity as a consequence of a low amount of localized states activated electrons contributing to the charge transport.

ACKNOWLEDGEMENT

This work has been supported by the Ministry fuer Forschung und Technologie; contr.no. 4045 B.

REFERENCES

/1/ D.E. Carlson, Sol. Energ. Mat., 3, 505 (1980)
/2/ R.C. Chittick, J.H. Alexander, H.F. Sterling, J. Electrochem. Soc.,116, 77 (1969)
/3/ W.E. Spear, P.G. LeComber, Sol. State Comm., 17, 1193 (1975)
/4/ D.E. Carlson, 3rd E.C. Photovolt. Sol. Energy Conf. Oct. 27-31, 1980, Cannes, France
/5/ D. Kaplan, N. Sol, G. Velasco, P.A. Thomas, Appl. Phys. Lett., 35, 440 (1978)
/6/ M.J. Thompson, J. Allison, M.M. Alkaisi, S.J. Barber, 1st E.C. Photovolt. Sol. Energy Conf., Sept. 27-31 1977, Luxembourg
/7/ T.D. Moustakas, D.A. Anderson, W. Paul, Sol. State Comm., 23, 155 (1977)
/8/ J. Bohdansky, J. Appl. Phys.,51, 2861 (1980)
/9/ G.H. Bauer, G. Bilger, Thin Solid Films, to be publ.
/10/ G.H. Bauer, G. Bilger, W.H. Bloss, Statusber. Sonnenenrg. II June 1980, VDI-Verlag, Düsseldorf F.R.G.
/11/ P.G. LeComber, W.E. Spear, Phys. Rev. Lett., 25, 509 (1970)
/12/ W.E. Spear, Proc. 5th Int. Conf. Amorph. Liqu. Semicond., 1973, Garmisch-Partenk., F.R.G.
/13/ P.J. Zanzucchi, C.R. Wronski, D.E. Carlson, J. Appl. Phys., 48, 5227 (1977)
/14/ W.T. Pawlewicz, J. Appl. Phys., 49, 5595 (1978)
/15/ R. Fischer, Amorph. Semicond., ed. by M.H. Brodsky (Springer Verlag, Berlin, New York, 1979)

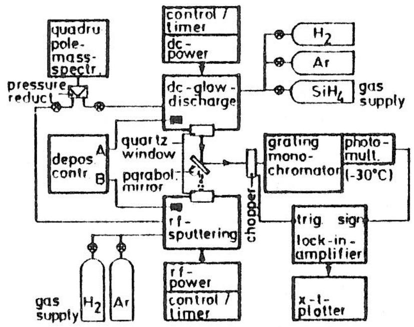


Fig.1 Experimental setup for a-Si:H preparation and plasma diagnostics

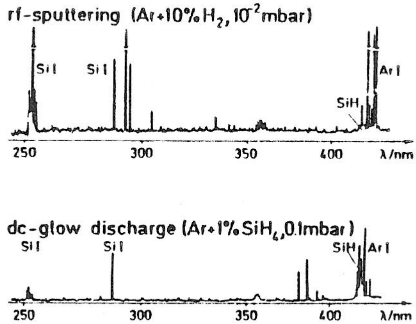


Fig.2 Optical emission spectra of discharges for a-Si:H preparation

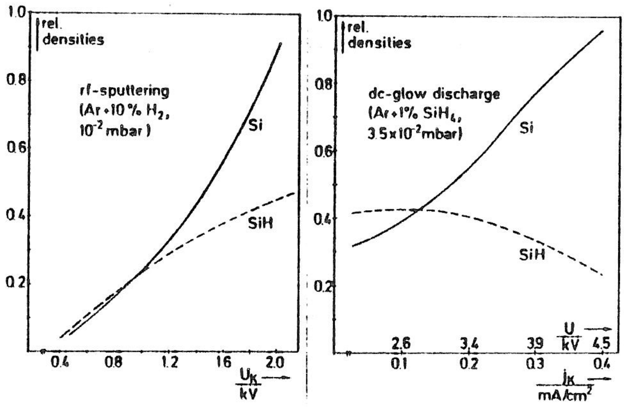


Fig. 3 Relative densities $n_{Si}$, $n_{SiH}$ generated in rf-sputtering and dc-glow discharge versus applied voltage resp. current density

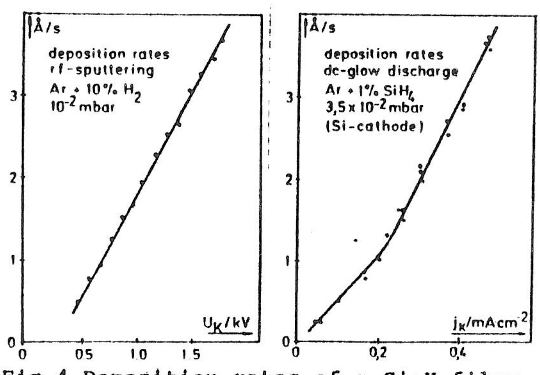


Fig.4 Deposition rates of a-Si:H films in rf-sputtering and dc-glow discharge vs. voltage/current dens.

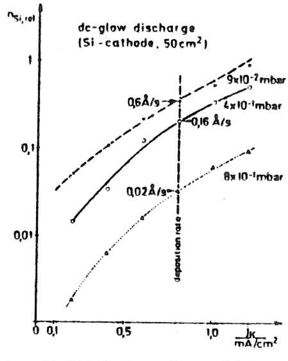


Fig.5 Relat. densities of Si in a dc-glow disch. generated by dc-sputtering effect

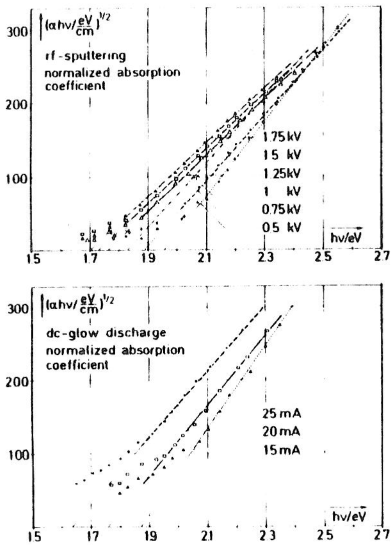


Fig.6 Normalized absorption coefficient of a-Si:H prepared by rf-sputtering and dc-glow disch., parameter: applied voltage/current density

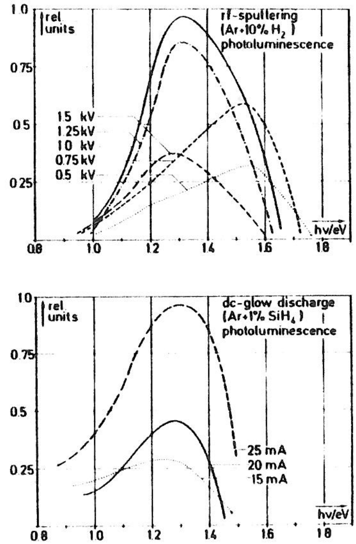


Fig.7 Relative yield of photoluminescence of a-Si:H prepared by rf-sputtering and dc-glow disch., parameter: applied voltage/current density

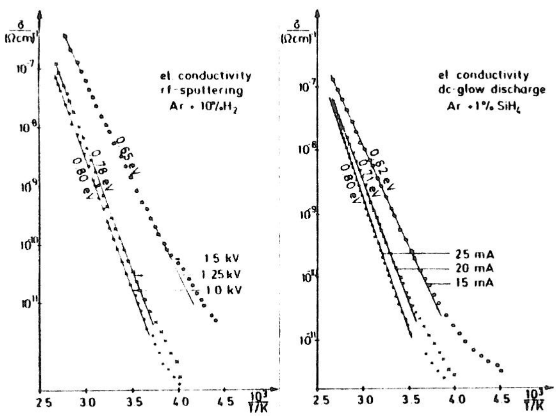


Fig.8 Temperature dependent electrical conductivity of a-Si:H prepared rf-sputtering and dc-glow disch., parameter: applied voltage/current density

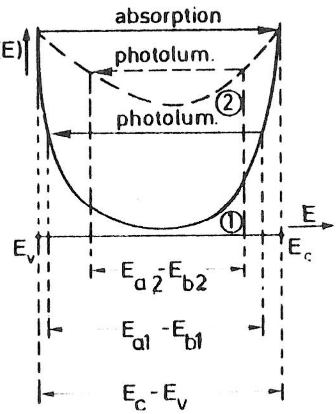


Fig.9 Schematic function of density of states (low 1, high 2)