INTRINSIC, n- AND p-DOPED a-Si:H THIN FILMS GROWN BY DC MAGNETRON SPUTTERING WITH DOPED TARGETS

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ABSTRACT

Intrinsic, n- and p-type a-Si:H films were deposited by dc magnetron sputtering and analyzed with several techniques. The films were synthesized in a reactive Ar-H_2 atmosphere giving H contents in the range of 3-20 at %. The films were sputtered from pure silicon targets and doped silicon targets with 1 at % B or P. Doping by co-sputtering from composite Si/B_4C targets was also explored. The doping concentrations were $3 \times 10^{20} - 2 \times 10^{21}$ cm^{-3} for the p-type films and 2.6-2.9 x 10^{19} cm^{-3} for the n-type films. The conductivity was in the range 10^{-2}-10^{-4} $\Omega^{-1}cm^{-1}$ for p-doped films and 10^{-5} $\Omega^{-1}cm^{-1}$ for the best n-doped films. Band gap estimations were obtained from dielectric function data and showed an increase with hydrogen content. A comparison to device quality PECVD-samples was also made.

INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) is used in a number of different applications, such as solar cells, thin film transistors for liquid crystal displays, image sensors for document scanning and medical X-ray imaging [1, 2]. Plasma enhanced chemical vapor deposition (PECVD) is the most frequently used technique for fabricating thin films of a-Si:H. However physical vapor deposition (PVD) has also successfully been used [3-6]. In many cases PVD is a superior technique due to the possibility to deposit films on substrates which must not be heated. PVD also allows modification of the growth conditions far from thermodynamic equilibrium.

This work investigates the possibilities to fabricate device quality intrinsic, n- and p-type a-Si:H by magnetron sputtering with the intention of making photo diodes for digital cameras. The n- and p-type doping is obtained by sputtering from P- and B-doped targets, respectively. Doping by co-sputtering from composite Si/B_4C targets was also explored. A comparison to device quality PECVD samples from Xerox PARC was made.

EXPERIMENTAL DETAILS

All films were grown in a planar magnetron sputtering system. The system consists of two 3 inch magnetrons placed in the top lid of a cylindrical chamber. An electrically isolated plate is placed between the magnetrons to avoid cross-contamination. There are shutters to both the magnetrons and the rotating substrate table. The samples were loaded through a load-lock. For the co-sputtered films a 2 inch magnetron was used.

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Before the films were grown, the system was evacuated to 5 x 10^{-7} Torr, using a turbomolecular pump and a titanium sublimation pump (TSP). Then the substrates were heated to 250°C, by a boron-nitride covered graphite heater placed in the substrate table. Thereafter, H_2 was introduced into the chamber to the desired partial pressure, and followed by 1.5 mTorr Ar, as measured by a capacitance manometer. The target current was kept constant at 0.2 A, giving a target voltage that varied between 450-500 V depending on target and H_2 pressure. The substrates were kept at a floating potential. During the deposition the TSP was operated in a continuous mode, to obtain more uniform hydrogen pumping speed. The deposition rate of the a-Si:H films was 33-100 Å/min depending on the hydrogen partial pressure.

A polycrystalline target of purity 99.999% was used for the intrinsic films. The partial pressure of the 99.9996% pure hydrogen gas was varied between 0.4 - 0.7 mTorr.

B- and P-doped targets of hot-pressed silicon with 1 at % B or P, respectively, were used for the doped films. The co-sputtered film was grown using a pure silicon target with a sector replaced by a piece of B_4C. The hydrogen partial pressure for both the doped series was varied in the range of 0.5 - 6 mTorr. The hydrogen concentration depth profiles were determined by nuclear reaction analysis (NRA) utilizing the $^1H(^{15}N, \alpha\gamma)^{12}C$ nuclear resonance reaction using the resonance at 6.385 MeV. The B- and P-concentration depth profiles were determined by secondary-ion mass-spectroscopy (SIMS) using calibrated standards as a reference.

Film thickness values were measured both by a Jeol JSM-T220A scanning electron microscope, a Dektak 3030 profilometer and Rutherford back scattering spectroscopy. The surface structure was analyzed by a Nanoscope IIIa atomic force microscope system, from Digital Instruments, operated in tapping mode using silicon cantilevers. The scanned area was typically 1 μm^2 from which the surface root-mean-square (rms) roughness was determined. The film microstructure was analyzed by a Philips CM 20 UT electron microscope operated at 200 kV, equipped with a LaB_6 filament, with cleaving as sample preparation method. The optical properties were determined by variable angle spectroscopic ellipsometry (SE) (VASE, J. A. Woollam Co.) in the photon energy range 1.24-5 eV.

The films analyzed with SIMS and SE were grown on float zone silicon wafers. For the electrical measurements oxidized silicon wafers were used. The P-doped films were also deposited on substrates with an aluminum stripe to ensure that the films have good adhesion to a metal contact. The PECVD material was grown on the same types of substrates (sent to the lab at Xerox PARC), as the sputtered films.

RESULTS AND DISCUSSION

The TEM picture in Fig. 1 shows one of the intrinsic films and displays that the film is dense and homogeneous, with no resolved microstructure. Contrary to the intrinsic film, the P-doped film in Fig. 2 shows a columnar structure and is micro crystalline. The TEM analysis of the P-doped film also showed that voids are present at the substrate/film interface.

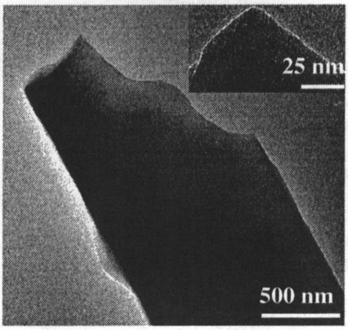

Figure 1. TEM image of intrinsic a-Si:H. The film thickness is 1.25 µm. The substrate is not visible in the picture.

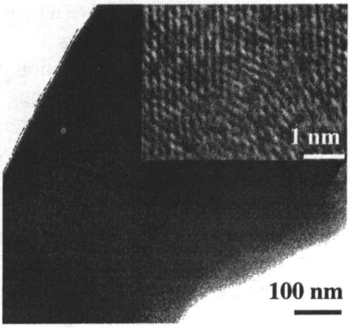

Figure 2. TEM image of P-doped a-Si:H. The film thickness is 0.53 µm. The film is grown on an oxidized silicon wafer and the silicon dioxide is visible to the right in the picture.

The surface structure of an intrinsic a-Si:H film, displayed in the AFM image in Fig. 3 shows a smooth film with an rms roughness of 2.6 nm for a film thickness of 1100 nm. The film is considered to be grown with small thickness variations, since the substrate is oxidized silicon with an rms roughness of 0.21 nm. The sputtered film does not differ significantly from the 600 nm thick PECVD-film in Fig. 4 which has an rms roughness of 1.4 nm. The thickness variations increase with thickness for the sputtered films while the roughness of the films is considered to be of comparable magnitude. The sputtered B-doped films are also smooth with rms roughness values of 0.8-1.1 nm, for 220-1100 nm thick films (Fig. 5). Both the intrinsic and B- doped films have a long range smoothness with peak-to-peak values of maximum 10 nm for B-doped samples and 25 nm for intrinsic a-Si:H.

The sputtered P-doped films, however, have in general larger rms roughness values in the range 3-6 nm for similar film thickness (Fig. 6). For some of the P-doped samples there are larger bumps with heights up to 60 nm separated by 100-200 nm. These thickness variations are considered to be connected to the columnar growth shown in the TEM picture in Fig. 2. The AFM results also indicate a connection of this type of growth to the hydrogen pressure, since the film grown at the lowest hydrogen partial pressure is more smooth.

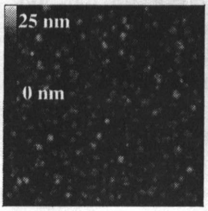

Figure 3. Sputtered intrinsic a-Si:H. Film thickness 1100 nm, rms roughness 2.6 nm.

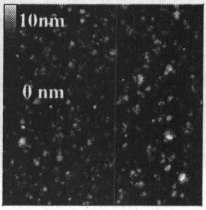

Figure 4. PECVD grown intrinsic a-Si:H. Film thickness 600nm, rms roughness 1.4 nm.

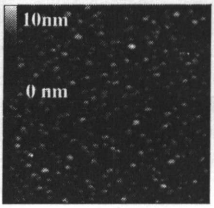

Figure 5. B-doped sputtered a-Si:H. Film thickness 1100 nm and rms roughness 1.1 nm.

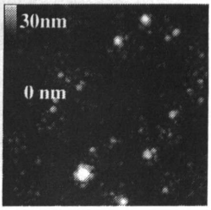

Figure 6. P-doped sputtered a-Si:H. Film thickness 500 nm, rms roughness 3.4 nm.

The NRA studies show that the intrinsic films have a hydrogen content of 10-30%. The B-doped and P-doped films have a hydrogen content of 2-6% and 11-18%, respectively, for similar hydrogen partial pressures.

The highest boron concentration was 2 x 10^{21} cm^{-3} and found in a co-sputtered film with a hydrogen content of 2.3%. Sputtering from a B-doped target yielded B-concentrations of 2.8 - 3.0 x 10^{20} cm^{-3}. The doping content in the P-doped films was 2.6 - 2.9 x 10^{19} cm^{-3}. The B- or P-contents in the measured films were not affected by the hydrogen partial pressures.

Results from the four-point probe measurements are displayed in Table I. The highest conductivity was 4.1 x 10^{-2} $ohm^{-1}cm^{-1}$ for one of the B-doped films sputtered from a doped target. The co-sputtered B-doped film with the higher B-concentration has a conductivity of 1.2 x 10^{-2} $ohm^{-1}cm^{-1}$, which can be explained by lower doping efficiency for highly doped films [4]. The measurements were not made in total darkness. A very weak background light was present. However, all films show higher conductivity when illuminated by a 20 W microscopy lamp focused on the samples. The intrinsic and P-doped samples show very low conductivity (only one P-doped sample had conductivity within the measurement range of the four-point probe). One reason for the low doping effect in the P-doped samples may be that most P-atoms become threefold-coordinated in the a-Si:H network [7]. This energetically favored configuration is not electrically active. Another possible explanation for the low conductivity in the P-doped samples is the columnar microstructure which can be seen in the TEM image in Fig. 2.

Table I: Results from measurements with four-point-probe.

	Conductivity ($ohm^{-1}cm^{-1}$)
B-doped sputtered (doped target)	4.1 x 10^{-2}
B-doped co-sputtered	1.2 x 10^{-2}
B-doped PECVD material	3.9 x 10^{-3}
P-doped sputtered (doped target)	2.0 x 10^{-5}
P-doped PECVD material	4.0 x 10^{-2}

From the spectroscopic ellipsometry data the dielectric function ε of the a-Si:H films was obtained. From ε the optical band gaps were calculated using Tauc plots [8]. Using the AFM rms roughness and peak-to-peak values, a correction for over-layers and film thickness variations was made before making the band gap estimations. A more detailed study of the optical properties for a P-doped film resulted in the real and imaginary parts of the dielectric function shown in Fig. 7. The parameters were extracted from the measured pseudo-dielectric function using a three layer model (over-layer/a-Si:H/SiO_2 oxide layer) where the layer thickness values and the dielectric function of a-Si:H were free parameters. The over-layer represents surface oxide and roughness and was modeled with a Bruggeman effective medium approximation mixing 50% a-Si:H and 50% voids. Solutions of the dielectric function of the a-Si:H films were determined for different values of the layer thickness. The physically most correct solution presented in Fig. 7 corresponds to the thickness values for which the dielectric function shows no features corresponding to the interference seen in the pseudo-dielectric function [9]. Some of the optical spectra for P-doped films have features corresponding to the E_1 and E_2 transitions in crystalline silicon [10] which is due to the fact that these films are micro crystalline. The optical properties of the film shown in Fig. 7 did not show effects of these transitions. The general finding is that the band gap increased with hydrogen content, as shown by others.

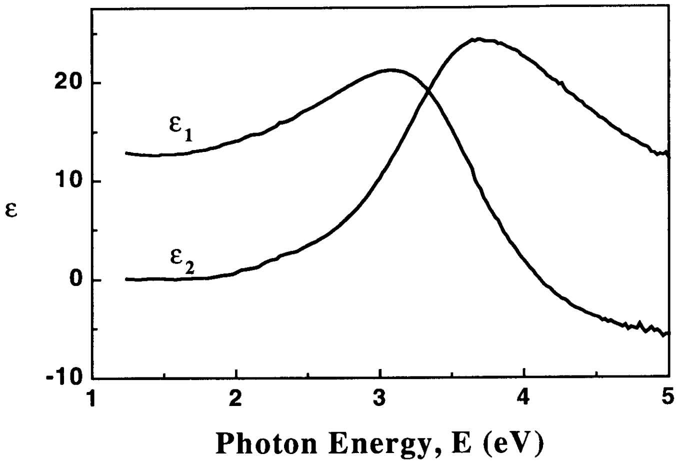

Figure 7. The complex dielectric function,
$\varepsilon = \varepsilon_1 + i\varepsilon_2$ of a P-doped a-Si:H film.

CONCLUSIONS

Successful p-type doping of a-Si:H films has been achieved by incorporation of boron in the films from a doped target as well as by co-sputtering of silicon and B_4C. Further work is needed for phosphorous doped n-type films to remove the columnar growth and increase the conductivity. The intrinsic films are highly resistive as expected.

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