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PHYSICAL PROPERTIES OF PHOSPHORUS DOPED LOW-PRESSURE CVD AMORPHOUS SILICON

G. Harbeke and A.E. Widmer

Laboratories RCA Ltd., Zurich Switzerland

J. Stuke

University of Marburg, F.R.G.

The growth of phosphorus doped a-Si films deposited by low pressure chemical vapor deposition and measurements of the spin density, electrical conductivity and optical band gap are reported. We conclude from the results that both defect compensation and substitutional incorporation of phosphorus occur.

Amorphous silicon films deposited by glow discharge (GD) decomposition of silane have been shown to have a low density of localized states in the energy gap [1] due to bonding of hydrogen to the majority of defects in the amorphous structure. Spear and Le Comber have demonstrated that the low gap state density also renders the GD film susceptible for substitutional doping by phosphorus or boron [2]. Later it was shown that substitutional doping of a-Si is possible in the chemical vapor deposition (CVD) process without the incorporation of hydrogen [3]. In this paper we report on the growth and the physical properties of phosphorus (P) doped a-Si films deposited by low pressure CVD (LPCVD).

The amorphous silicon films were prepared in a low pressure reactor [4] by thermal decomposition of a silane-phosphine gas mixture. The system pressures were typically 500 mTorr, the deposition temperature $565^{\circ}C$ and the total gas flow 100 to 120 cm³ min⁻¹. The gas flow ratio PH₃/SiH₄ was varied from 2×10^{-5} to 6×10^{-3} . Two phosphine doping gas mixtures of 0.1 and 1% in nitrogen were used in addition to concentrated silane. Films ranging from 0.3 to 0.5 μ m thickness were deposited on sapphire, molybdenum and quartz substrates. The structure of the films was investigated by Raman scattering (E.F. Steigmeier). There is a sharp transition in growth temperature at 575°C where the structure changes from the amorphous to the crystalline phase.

The growth rates were determined on films deposited on sapphire substrates with a Dektak surface profile monitor. Aluminium contact structures were evaporated in order to measure the lateral dark- and photoconductivity. The geometry of the contact formed a gap-cell with a width of 50 µm and a length of 6 mm.

Electron spin resonance (ESR) was measured with a Varian El2 spectrometer in the X-band (9.2 GHz). The optical absorption coefficient K was determined by measuring transmission and reflection of the layers in the wavelength range from 0.4 to 1.8 μ m and evaluating the data in terms of the formulas for multiple reflection and transmission.

Fig. 1 shows the growth rate as a function of gas flow ratio. We observe a weak variation of the growth rate with a minimum around a ratio of $3 \cdot 10^{-4}$ and a maximum at about $8 \cdot 10^{-4}$. This result is in contrast to CVD deposition at T_s = 650° C where the growth rate is nearly 300 R/min for undoped or slightly doped



Fig. (1) Growth rate of phosphorus doped a-Si vs. gas flow ratio

material and steeply decreasing starting at a ratio of $4 \cdot 10^{-4}$ [3]. Also, we find that the upper temperature limit for deposition of the amorphous phase is 575°C in LPCVD whereas the crystallization temperature in CVD is 675°C [5].

The phosphorus concentration N_p in the films was determined by Secondary Ion Mass Spectroscopy (SIMS) by C.W. Magee, RCA Laboratories, Princeton. It was found to be nearly proportional to the gas flow ratio. At a ratio of 10^{-2} a concentration of 2.10^{21} P atoms / cm³ equivalent to a P / Si ratio in the film of 4.10^{-2} was measured. The H / Si ratio is below 5.10^{-3} in all films independent of N_p.

Fig. 2 shows the spin density N_S as measured by ESR as a function of the gas flow ratio. We observe a steep decrease of N_S starting at about 4.10^{-4} . The g-value is 2.0055 independent of N_S and the peak-to-peak linewidth Δ Hpp decreases from 9.5 G for N_S = 4.1017 cm⁻³ to 4.65 G for N_S = 1019 cm⁻³. This g-value and the correlation between N_S and Δ Hpp are in agreement with ESR data obtained from a-Si prepared by other methods [6]. Fig. 3 shows the dc conductivity as a function of gas flow ratio. The dark conductivity σ_D first decreases with increasing ratio to a flat minimum at 4.10^{-4} . For higher ratios there is a steep increase of σ_D to a maximum of $2\cdot10^{-1}$ (Ω cm)⁻¹ for $6\cdot10^{-3}$. The photoconductivity σ_{Ph} , measured under AM1 conditions, follows the increase of σ_D and goes up to 10^{-3} (Ω cm)⁻¹. Fig. 4 shows the effective energy gap obtained by extrapolation of plots of (K·E)^{1/2} vs. E to the abszissa where E is the photon energy. The gap value for low doping is 1.61 ± 0.01 eV and it increases to 1.67 eV for N_p = 2.10^{21} cm⁻³.

The ESR properties of undoped or slightly P-doped LPCVD a-Si are very similar to those of a-Si deposited by other techniques in the absence of hydrogen. The small hydrogen content of less than 0.5% is not sufficient to reduce the spin density N_s to below 10^{19} cm⁻³. The strong increase in σ_D with increasing PH₃/SiH₄ ratio shows that substitutional doping is nevertheless possible by phosphorus alone, i.e. without the simultaneous incorporation of additional hydrogen. Concurrently with the increase of σ_D at a gas flow ratio of 10^{-3} we observe a steep decrease of N_s . There are two possible mechanisms to explain this reduction: (i) direct defect compensation by phosphorus atoms through formation of a complex thereby eliminating dangling bonds. Such a model has been invoked for P-doped CVD a-Si by Hirose et al. [5]. (ii) direct "brute force" doping by substitutional replacing of a silicon by a phosphorus atom. The extra donor



Fig. (2) Spin density of phosphorus doped a-Si vs. gas flow ratio

Fig. (3) Dark (σ_D) and photoconductivity σ_{Ph} of phosphorus doped a-Si vs. gas flow ratio

electron can be captured by a dangling bond state thereby making the center dia-magnetic. It should be noted that the phosphorus concentration, at which N_s starts to fall is about one order or magnitude larger than the original spin



Fig. (4) Effective band gap of phosphorus doped a-Si vs. gas flow ratio

density. This is not unlike the situation in a-SiH $_{\rm X}$ where the H-concentration which is required to saturate the dangling bonds is much higher than the spin density without hydrogen.

The minimum in the dark conductivity at $N_p = 10^{20} \text{ cm}^{-3}$ is not caused by compensation since the undoped films are already n-type. The same effect was found in CVD a-Si where it has been explained by a reduction of the hopping conductivity [3]. Since the conduction mechanism for slightly doped LPCVD is most probably also by hopping via gap states, this result supports the assumption that at least part of the phosphorus atoms act as direct defect compensators. This occurs in the range N_p = 10^{19} to $10^{20}~{\rm cm}^{-3}$ where the spin density is still at its original high level. It seems that only spin-inactive centers are compensated in this range. It is interesting to note that the minima in conductivity and growth rate (see Fig. 1) occur at the same phosphorus concentration. One could be tempted to suppose a correlation between the compensation mechanism and the growth kinetics.

The steep increase of σ_D starts at concentrations where N_S decreases. There is little doubt that in this range also substitutional doping occurs which can compensate spin-active centers through the second process. So both processes may work in parallel and at this point no quantitative statements can be made as to their relative strength.

The increase in band gap for $N_p = 2.10^{21} \text{ cm}^{-3}$ over the value for undoped or slightly doped material is 0.06 eV. This increase is about the same as in a-SiH for a comparable H concentration [7]. In a-SiH_x it is generally explained by the fact that the Si-H single bond energy (72 kcal/mol) is considerably larger than the Si-Si single bond energy (54 kcal/mol). This argument does not hold for a-SiP_x since the Si-P single bond energy is 50 kcal/mol[8]. In this case we have to look for a different mechanism causing a strong modification of the joint density-of-states distribution at energies above ${\rm E_g}$ upon incorporation of phosphorus. Spear et al.[9]have investigated amorphous phosphorus films and estimated a band gap value of 2.5 to 3 eV. For the same system $a-SiP_X$ some variation between the values of the two constituents is to be expected. In amorphous Si-Ge alloys a linear variation with composition was observed [10]. A linear variation in a-SiP_x would give a shift of 0.04 to 0.06 eV for N_p = 2.10^{21} cm⁻³ which is in good agreement with the experimental value of 0.06 eV.

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