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DOPING EFFECTS IN CVD DEPOSITED AMORPHOUS SILICON : A STUDY BY LIGHT-INDUCED ESR

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A study of light-induced ESR in CVD deposited amorphous silicon doped with phosphorus is presented. The effect is interpreted in terms of light-induced *increases and decreases* of the ESR signal. A negative signal for boron doped samples is also reported for the first time.

Preparation of amorphous silicon by Chemical Vapor Deposition (CVD) has been the subject of several recent reports [1,2,3]. This process differs from the more common glow discharge deposition technique in that the decomposition of Silane to produce Silicon is not plasma assisted but thermally assisted. The range of deposition temperatures is relatively narrow, being limited on the high temperature side by the crystallisation limit (around 650°C) and on the low temperature side by the rapid *decrease* of decomposition rate with *decreasing* substrate temperature. A typical decomposition temperature is 600°C. At this temperature, hydrogen is not stable in silicon so that the hydrogen content of the film is low, typically of the order of 3 atoms per 1000 silicon atoms [4]. As a consequence, the films contain a relatively large quantity of unsaturated dangling bonds, of the order of 10^{19} per cm^3, more than two orders of magnitude in excess of common values for glow discharge produced films. It has been shown that, in contrast to non hydrogenated amorphous silicon produced by evaporation, it is possible to get very large *increases* of conductivity by doping [1,3]. The maximum values of conductivity obtained are even larger than for films produced by the glow discharge process, a fact which has no clearcut interpretation at present.

We present here a study of the Electron Spin Resonance (ESR) under visible light irradiation of doped CVD films. The motivation for this study was two-fold :

a) we wanted to get insight on the doping mecanism. Light induced ESR is a means to investigate the nature of the defect electronic levels, in particular dangling bond related levels

b) what we would learn about dangling bonds in the films produced by CVD, in which they are numerous, could presumably be applied to understand how residual dangling bonds may affect the films produced by glow discharge decomposition.

Films have been prepared in a conventional CVD system at 600°C and atmospheric pressure. Hydrogen was used as a carrier gas. Doping was accomplished by mixing variable proportions x of phosphine (PH_3) for n-type doping and diborane (B_2H_6) for p-type doping.

Fig.(1) shows the conductivity at room temperature and the density of spins measured in the dark at T=90 K. One distinguishes two doping ranges :

a) Below $x=3\cdot10^{-4}$ the conductivity is doping independent. The ESR spectrum consists of a line with g-value of 2.0055 characteristic of a dangling bond in its neutral charge state. The spin density *decreases* with *increasing* doping, vanishing at the limit concentration of $x=3\cdot10^{-4}$.

b) Above this concentration, one observes a sharp *increase* of conductivity with doping. Also a new ESR line with lower g-value (g=2.004) appears. Its intensity *increases* rapidly with doping up to concentrations x of order 10^{-3} then tends to *decrease*.

X-ray diffraction shows no sign of crystallisation which could account for the change of properties with doping. Similar results have been reported by Taniguchi et al. [1] and Hazegawa et al. [5]. They can be interpreted in the following simple way :

The dangling bonds introduce two sets of levels in the a-Si pseudo-gap. The lower level D^0 corresponds to a neutral charge state. The dangling bond in this state is paramagnetic and yields the g=2.0055 ESR line. The upper level corresponds to a negatively charged state D^-. It is non paramagnetic. In addition, one assumes the existence of states below the conduction band mobility edge, loosely called conduction band tail states. As the doping is *increased* the D^0 levels become progressively filled with donated electrons and the dangling bond ESR *decreases*. The conductivity remains constant since : a) the Fermi level is pinned between the D^- and D^0 levels, and b) conduction proceeds by hopping near the Fermi level. Above $x=3\cdot10^{-4}$ the ESR data indicates that the D^- level is completely filled. The Fermi level now moves up with *increasing* doping, the donated electrons filling the conduction band tail states, where they give rise to the g=2.004 signal.

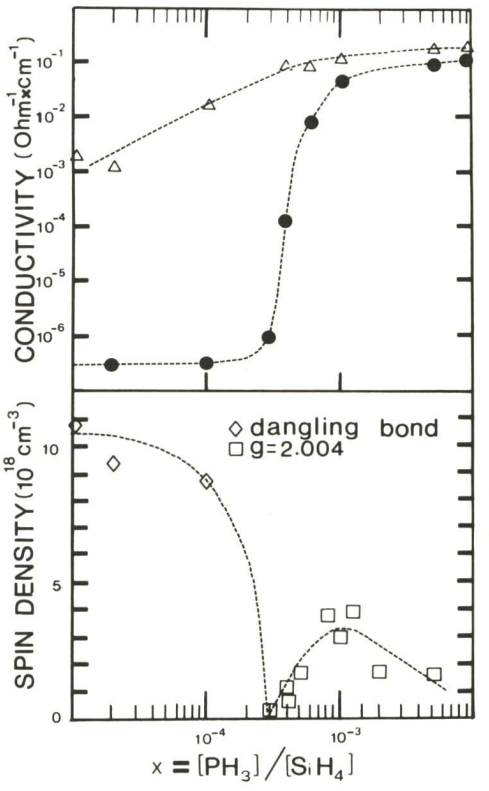

Fig. 1 Room temperature conductivity (top) and spin density (bottom) as a function of phosphine concentration in the gas phase. The lozenges and squares refer to data for the two distinct resonances discussed in the text. The circles are conductivity data for the as-deposited specimens. The triangles refer to the same specimens after plasma hydrogenation, which eliminates Fermi level pinning by dangling bond levels. ESR was not detectable in the dark for plasma hydrogenated samples of less than $3\cdot10^{-4}$ phosphine concentration.

This picture is further confirmed by the effect of a hydrogenation post-treatment performed under a Hydrogen plasma. At low values of x, the dangling bond ESR signal disappears upon hydrogenation [3], whereas at values of x above $3 \cdot 10^{-4}$ the conduction band tail signal *increases*.

ESR experiments under visible light irradiation have been performed using a procedure described previously [6]. Low microwave powers of order .2mW are used, and systematic checks are performed to insure the absence of saturation. The light induced signal is defined as the difference between the spectrometer output under irradiation and in the dark. In a previous publication, we described the effect of light on undoped CVD samples. The irradiation resulted in a *decrease* of the dangling bond ESR signal, which was attributed to trapping of electrons and/or holes at dangling bond sites converting D^0 charge states into non paramagnetic D^- and D^+ charge states [7]. This type of behaviour prevails for all concentrations below the $x=3 \cdot 10^{-4}$ limit. Above this limit, we observe a signal *increase* upon irradiation. This is shown in Fig.(2) for a sample doped at $x=10^{-3}$. The ESR in the dark corresponds to the g=2.004 conduction band tail line discussed above. Under light irradiation the induced signal is shifted to lower field compared to the signal in the dark. Its center is close to the dangling bond ESR signal position. There is some tailing of the line to higher field, i.e. lower g-value. We interpret this result as follows : at high values of x, all dangling bonds have been converted to the D^- state. Upon light irradiation, holes are trapped by these negatively charged centers, which are converted to their paramagnetic charge state producing an *increase* of the dangling bond signal. The corresponding electrons are presumably trapped in the conduction band tail states, which may account for the tailing of the line at high field.

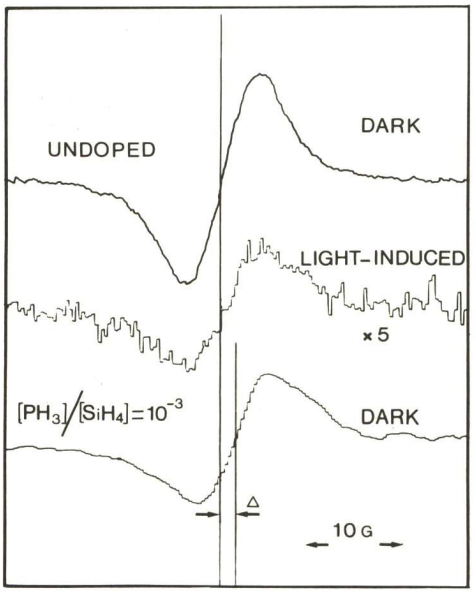

Fig. 2 ESR spectra at T=90K, 0,2 mW microwave power, 9.1 GHz frequency, top : undoped film, bottom : doped film in the dark, middle : light induced ESR for the doped film. The shift between the light induced and in the dark signals is approximately 2G.

Fig.(3) summarizes the magnitude and sign of the light induced signal, as a function of dopant concentration. The positive effect observed above the limit $x=3 \cdot 10^{-4}$ is maximum for dopant concentration in the vicinity of $x=10^{-3}$. The *decrease* at higher concentrations is presumably related to the *decrease* of the lifetime of the trapped hole for *increasing* electron concentration in the conduction band tail.

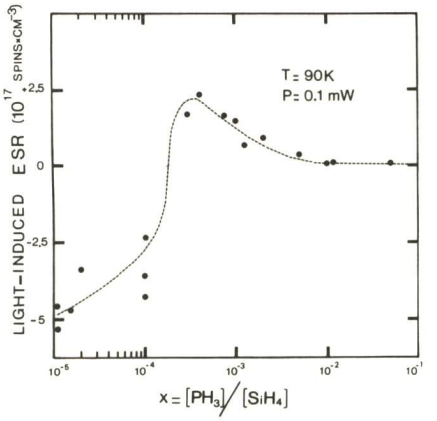

Fig. 3 Amplitude of the light induced ESR, for a fixed irradiation intensity from a tungsten-halogen lamp, as a function of phosphine content in the gas phase: Note the sign change above $x=3.10^{-4}$.

Our results point to a simple charge compensation of the dangling bond occuring with phosphorus doping, as opposed to a model where the effect of phosphorus would be to chemically tie the dangling bonds. Street et al. [8] have postulated a similar model to the one presented here to explain their results on light induced ESR in films grown by the glow discharge process. The data presented here supports their interpretation and indicates that non passivated dangling bonds are probably an important factor for the properties of glow discharge produced films.

We finally describe briefly the behaviour of Boron doped samples. The conductivity and ESR in the dark show a very similar pattern with a transition between a low doping region where the conductivity is small, the ESR in the dark originates from dangling bonds and the light induced ESR consists of a *decrease* of the dangling bond signal, and a high doping region, above $x=10^{-5}$, where the conductivity *increases* and the ESR signal in the dark consists of a broad line shifted to lower field values ($g=2.013 \pm 0.001$). Three features however are different :

a) the maximal value of the ESR signal corresponds to a spin density 3 to 4 times higher than for the phosphorus case.
b) Hydrogenation has little effect on either the conductivity or the spin signal
c) the light induced ESR corresponds to a *decrease* of this resonance in the dark. The effect is large : reduction of the signal by as much as 30% have been observed.

The interpretation of this behaviour is unclear at present. Generally speaking it probably implies that the states involved above the valence band have a more pronounced localized defect character. The insensitivity to hydrogenation however indicates that they are not dangling bond related.

References

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