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MAGNETIC FIELD DEPENDENCE OF THE PHOTO- AND DARK CONDUCTIVITY IN DOPED a-Si:H FILMS

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Abstract.- We have studied the influence of magnetic field on the photo-conductivity \( \sigma_{ph} \) and dark conductivity \( \sigma_d \) of glow discharge deposited a-Si:H films doped with phosphorus or boron up to a nominal content of 7 %. The relative change of \( \sigma_{ph} \) is of the order of \( 10^{-4} \) to \( 10^{-2} \) depending on temperature and on the dopant concentration. Its dependence on magnetic field strength \( B \) varies significantly with the position of the Fermi level. In highly doped material (\( B_{ph}/\sigma_{ph} > 10^{-3} \) and \( B_{ph}/\sigma_{ph} > 10^{-2} \)), we observe for the first time in this material - magnetic field induced changes of \( \sigma_d \). This magnetoconductivity effect is attributed to a second current path in localized band tail states close to the Fermi level.

Introduction.- Recently we found that the photoconductivity \( \sigma_{ph} \) of glow discharge deposited a-Si:H films changes by as much as 2 % if a magnetic field \( B < 10 \) kGauss is applied\(^1,2\). The dependence of \( \Delta \sigma_{ph}/\sigma_{ph} \) on \( B \) is anomalous and strikingly similar to the magnetoresistance effect previously observed in the variable range hopping regime of evaporated a-Si and a-Ge\(^3,4\). Both effects have been successfully interpreted in terms of a model by Movaghar and Schweitzer\(^5,6\), in which the recombination rate or hopping rate, respectively, depend on the spin relaxation rate which in its turn is modified by the applied field.

Our previous studies of \( \sigma_{ph} \) (B) were restricted to undoped\(^1\) or lightly doped\(^2\) a-Si:H films. Here we report an extension of these investigations to boron and phosphorus contents up to nominally 7 %. In the course of this study we also found that the dark conductivity \( \sigma_d \) is influenced by the magnetic field if the dopant content exceeds a certain limit (\( 10^{-3} \) for boron and \( 10^{-2} \) for phosphorus).

Experimental.- The a-Si:H films were deposited onto fused quartz substrates mounted at the grounded anode of a capacitively coupled glow discharge system. \( \text{SiH}_4 \) gas was premixed with \( \text{PH}_3 \) or \( \text{B}_2\text{H}_6 \) and diluted at a ratio of 1:1 with Ar. Pressure during deposition was 0.6 mbar, deposition rate \( \sim 3 \) \( \text{A/s} \) and substrate temperature \( 280^\circ \text{C} \). \( \sigma_d \) and \( \sigma_{ph} \) were measured by means of two evaporated Cr electrodes, 0.5 mm apart. To determine the dependence of both quantities on the magnetic field strength \( B \) we used a sawtooth type field generated by chopping the magnet current at a frequency of 1.5 Hz. The resulting change of the specimen current was amplified and monitored with a storage oscilloscope. Photoconductivity measurements were made with illumination by a tungsten-iodine lamp at an incident power of \( \sim 50 \) mW/cm\(^2\). In order to avoid changes of \( \sigma_{ph} \) during optical exposure (Staebler-Wronski effect?) the samples were illuminated for \( \sim 12 \) hours prior to the measurements. Some checks indicated that this treatment did not significantly change the dependence of \( \Delta \sigma_{ph}/\sigma_{ph} \) on \( B \) and \( T \).
Fig. 1: The relative change of the photoconductivity, $\Delta \sigma_{ph}/\sigma_{ph}$, as a function of magnetic field $B$ for various temperatures. The doping ratio is a) $[PH_3]/[SiH_4]=10^{-4}$ and b) $[B_2H_6]/[SiH_4]=10^{-4}$.

Results.- Fig. 1 compares the influence of magnetic field $B$ on the photoconductivity $\sigma_{ph}$ in two a-Si:H films doped with nominally the same content (10$^{-4}$) of phosphorus or boron. Plotted is the relative change of $\sigma_{ph}$ as a function of $B$ for various temperatures $T$. Other properties (e.g. thermopower and temperature dependence of $\sigma_{ph}$) clearly indicate that the charge carriers are electrons in Fig. 1a and holes in Fig. 1b. The behaviour seen in Fig. 1a is very similar to that previously reported for undoped a-Si:H which usually is also n-type. Both specimens in Fig. 1 show complicated, anomalous dependencies which are similar at low temperatures ($T<120$ K in Fig. 1a) but markedly different above 150 K. In order to ease the discussion we regard the experimental curves as being composed of a positive component $e_1$ and a negative component $e_2$ as indicated by the dashed curves in Fig. 1a ($T=100$ K). Obviously in Fig. 1a the component $e_1$ decreases much stronger with increasing temperature than $e_2$, whereas in Fig. 1b $e_1$ and $e_2$ decrease at a more similar rate.

The behaviour of n-type films is appreciably different from that in Fig. 1a if the PH$_3$ content lies in the range 3·10$^{-4}$ to 10$^{-2}$. This is demonstrated by the curves in Fig. 2a measured for a sample which was deposited at a gas doping ratio $[PH_3]/[SiH_4]=10^{-3}$. Here the negative component $e_2$ is small compared to $e_1$, the latter being of similar magnitude as in Fig. 1a. In contrast to this strong change for n-type films the behaviour of p-type specimens does not significantly vary in the doping range investigated (cf. Figs. 1b and 2b).

When the dopant content exceeds a certain limit ($[B_2H_6]/[SiH_4]=10^{-3}$ and $[PH_3]/[SiH_4]=10^{-2}$) also the dark conductivity $\sigma_d$ of our a-Si:H films is affected by the magnetic field $B$. Two typical examples of the dependence of $\Delta \sigma_d/\sigma_d$ on $B$ and on the temperature $T$ are shown in Fig. 3. The dopant content is 3 % for both the phosphorus doped film (Fig. 3a) and the boron doped film (Fig. 3b). It is interesting to note that the curves in Fig. 3 are very similar to those in Fig. 2 but opposite in sign. The magnitude of the components $e_1$ and $e_2$ determined at $T=150$ K is plotted in Fig. 4a as a function of the dopant content. Both components seem to saturate at high doping levels and steeply decay towards low doping ratios.
Discussion.— Before explaining the experimental results we briefly summarize our previously published model for magnetic field dependent recombination.\(^1\) We assume that, at least for part of the recombination processes, the rate limiting step is a transition of an electron (or hole) from a singly occupied localized state (e.g. a tail state) to another one which already carries a spin (e.g. a neutral dangling bond). If the spin flip or relaxation rate \(W\), in both centers, is smaller than the recombination rate \(R\), the latter depends on the spin configuration in the pair of initial states. Of particular importance are those pairs having triplet character (parallel spins). They can only recombine if one of the two spins flips before the pair dissociates. The dependence of \(W\) on the applied field \(B\) leads to a relative change of the photoconductivity \(\Delta\sigma_{\text{ph}}/\sigma_{\text{ph}}\) of the type described by eq. (1).

\[
\Delta\sigma_{\text{ph}}/\sigma_{\text{ph}} = \frac{H_I^2}{B^2} \frac{H_O^2}{H_O^2 + v^2} \quad (1)
\]

where \(H_I\) is the internal anisotropy field due to dipolar and hyperfine interactions and \(H_O\) is the external field \(B\), both expressed in frequency units (\(1 \text{ G} \equiv 2.8 \times 10^6 \text{ Hz}\)). The quantity \(b\) is a measure of the g-tensor anisotropy which is assumed to be proportional to the g-shift \(\delta g\) (\(b^2 = 3/10 \delta g^2\)), \(v\) is the frequency of fluctuations of the anisotropy fields and \(d\) is the dissociation or thermal release rate. For simplicity we have used here the approximation \(v \gg d \gg W\).

Relation (1) explains two features of the experimental results: i) \(\Delta\sigma_{\text{ph}}/\sigma_{\text{ph}}\) can be either positive or negative depending on whether \(H_I/v > b\) or vice versa, and ii) it saturates for \(H_O \gg v\). Two other important features of the experimental curves are the simultaneous occurrence of positive and negative contributions \((e_1, e_2)\) and the anomalous linear or sublinear dependence on \(B\) at small magnetic fields. They become plausible effects of the type described by eq. (1). Therefore, eq. (1) can only be used for a qualitative discussion of the experimental data.

The above model of spin dependent transitions was first used to explain the magnetic field induced changes of \(\sigma_d\) in evaporated a-Si and a-Ge.\(^5\) In these materials an appreciable contribution to \(\sigma_d\) is due to hopping processes in the localized states near the Fermi level. If the final state of a hopping transition is doubly
occupied, the rate of this transition, \( r_T \), is affected in the same way as the recombination rate of triplet pairs, \( R_T \). Since \( q_d \) increases with increasing \( r_T \) whereas \( \alpha_{ph} \) decreases with increasing \( R_p \), the changes of \( q_d \) and \( \alpha_{ph} \) must be opposite. This is just what we observe for highly doped a-Si:H films (cf. Figs. 2 and 3).

In weakly doped n-type films the negative component \( e_2 \) of \( \Delta \alpha_{ph}/\alpha_{ph} \) becomes stronger compared with the positive component \( e_1 \) when the temperature increases (Fig. 1a). This behaviour indicates that the distribution of the fluctuation frequency \( \nu \) changes with temperature such that the centroid shifts to larger values. For p-type films, on the other hand, this shift seems to be less pronounced, since the ratio of \( e_2 \) and \( e_1 \) varies only little with temperature. The reason for this different behaviour is not yet understood.

The most striking result of the present study is the strong decrease of the negative component \( e_2 \) when the phosphorus content exceeds \( 3\times10^{-4} \) (cf. Figs. 1a and 2a). We attribute this effect to a change of the predominant recombination channel. At the lower doping levels the recombination rate presumably is limited by a transition from a localized tail state to a singly occupied dangling bond state. At the higher doping ratios (\( \chi > 3\times10^{-4} \)) the Fermi level \( E_F \) lies in the band tail above the dangling bond levels, so that the recombination rate is determined by a transition from a localized state in the upper part of the tail to another one near \( E_F \) which is singly occupied. This latter assignment is supported by recent ESR data, which indicate that the g-tensor anisotropy of electrons in the conduction band tail, and therewith the quantity \( b \) in eq. (1), is smaller than that of the dangling bond electrons. As a consequence, the negative component \( e_2 \) should be smaller if the final state of the transition is a doubly occupied tail state instead of a dangling bond state, in agreement with our experimental results (cf. Figs. 1a and 2a). For p-type films we do not observe a significant change in the dependence of \( \Delta \alpha_{ph}/\alpha_{ph} \) on \( B \) with the dopant content, indicating that there is no marked change of the anisotropy of the g-tensor.

In undoped and weakly doped a-Si:H films \( E_F \) lies in an energy range where the density of states \( g(E) \) is so small that the charge transport in these states does not yield a noticeable contribution to \( q_d \). This situation changes when, due to doping, the Fermi level \( E_F \) is shifted into a region of larger \( g(E) \). The results in Fig. 4a indicate that, for boron doped films, hopping near \( E_F \) contributes significantly to \( q_d \) (at \( T=150 \) K) if the dopant content exceeds \( 10^{-3} \). In phosphorus doped films this occurs only at an appreciably higher doping ratio (\( > 10^{-2} \)). This result reflects the large asymmetry in the effective density of gap states indicated by field effect data. We believe that the magnetic field dependent processes are hops from singly occupied tail states to other singly occupied tail states. The striking similarity of \( \Delta q_d/q_d \) with \( -\Delta \alpha_{ph}/\alpha_{ph} \) in highly doped films (cf. Figs. 2 and 3) suggests that such inter-tail transitions also determine the recombination rate in these films.

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