PHILOSOPHICAL MAGAZINE B, 1983, VOL. 48, NO. 6, 561–569

Hydrogenation and direct-substitutional doping of evaporated amorphous silicon films

By S. ISELBORN, H. RÜBEL, J. GEIGER and B. SCHRÖDER
Fachbereich Physik, Universität Kaiserslautern,
D-6750 Kaiserslautern, F.R. Germany

[Received 24 May 1983 and accepted 1 August 1983]

ABSTRACT

The addition of hydrogen during the evaporation of silicon has been shown to improve the electrical properties of the resulting a-Si film considerably by saturation of dangling bonds, if molecular dissociation takes place. Evaporation onto a substrate at room temperature and subsequent annealing has been shown to yield a film with a high resistance. It has been found that preparation at elevated substrate temperatures improves the photoconductivity further, and that adding phosphine to the hydrogen atmosphere during the evaporation produces efficient phosphorus doping.

§ 1. INTRODUCTION

Previous studies of the electrical conductivity of evaporated amorphous silicon films (ev-a-Si) (Grigorovici, Croitoru and Devenyi 1967, Brodsky, Title, Weiser and Petit 1970, Lewis 1972, Beyer and Stuke 1975) showed that the resulting films were characterized by a high density of defect states within the forbidden gap between the conduction and valence bands. This has been proved quantitatively by Spear (1977) and others, and was assumed to be the reason why ev-a-Si could not be doped. On the other hand, a-Si can be prepared by decomposing silane in a glow discharge (gd-a-Si : H) with an extremely low density of states within the gap, resulting from saturation of the electrically active defects with hydrogen, and therefore doping is possible (Spear and Le Comber 1975). Hydrogenated sputtered amorphous silicon (sp-a-Si : H) is obtained by admixture of hydrogen to the argon sputtering gas, and doping of sputtered hydrogenated silicon is also possible (Paul, Lewis, Connell and Moustakas 1976).

The successful preparation of dopable a-Si by glow-discharge decomposition and by sputtering lessened the interest in evaporated material. Recently, however, several research groups have made efforts to passivate the electrically active defects in evaporated films by various auxiliary methods of preparation. Malhotra and Neudeck (1976) evaporated silicon in an atmosphere of molecular hydrogen, and the resulting film was annealed at 400°C. Depending on the partial pressure of the molecular hydrogen, the defect density in the gap could be more or less reduced, which manifests itself by an increase in the electrical resistivity. Kaplan, Sol, Velasco and Thomas (1978) prepared samples with strongly reduced ESR signals (arising from dangling bonds) by a subsequent treatment of the evaporated films in a hydrogen plasma. Miller, Lutz,

Wiesmann, Rock, Ghosh, Ramamoorthy and Strongin (1978) reported that the room-temperature dark conductivity was reduced by six to eight orders of magnitude if atomic hydrogen was mixed with the stream of evaporated silicon. Jang, Kang and Lee (1980) succeeded in reducing the room-temperature conductivity by means of a subsequent diffusion of hydrogen into the sample from a surrounding hydrogen gas discharge. Measurements reported by Kniffler, Müller, Pirrung, Hänisch, Schröder and Geiger (1981) showed that the room-temperature dark conductivity $\sigma_{D,RT}$ of pure silicon films prepared at low temperatures decreases with increasing annealing temperature because of structural relaxation processes. The value $\sigma_{D,RT} = 10^{-7}\ \Omega^{-1}\ cm^{-1}$, however, seems to be a lower limit. Only if molecular hydrogen was added during the evaporation, could a considerably lower value of the dark conductivity be observed for ev-a-Si prepared at a substrate temperature $T_S = 10$ K.

§ 2. Experimental methods

The ev-a-Si films were prepared in an ultra-high vacuum system equipped with an electron gun evaporation source. The evaporated materials were differently doped single-crystal silicon, the original doping apparently having no noticeable influence on the properties of the evaporated films. In the present study the base pressure of the vacuum system was 2×10^{-8} Torr. This pressure increased during evaporation to 8×10^{-8} Torr. The deposition rate of the films was 1–3 Å s^{-1}, the thickness of the films being 3000 Å. Hydrogen and phosphine could be introduced independently of each other through two needle valves into the vacuum system. In addition it was possible to dissociate the admitted gases by using various heated tungsten filaments (' dissociators '). The diameter of the heating wire used was 0·2 mm. The filaments were placed 5 cm from the substrates in line of sight with the growing film. They were heated to about 2300 K. The degree of dissociation during the individual evaporation runs was presumably different and of the order of a few per cent. It was checked by helium back-scattering experiments that the resulting silicon films did not contain tungsten evaporated from the dissociator. As long as contamination was avoided, the properties of the films did not depend sensitively on the particular form of the filament. The base pressure increased by about one order of magnitude after hydrogen was introduced into the vacuum system, as measured with a quadrupole mass analyser.

The substrate holder was able to revolve so that up to eight samples could be prepared under different conditions without breaking the vacuum. Hence these eight samples should have the same properties with respect to the pressure and the composition of the background vacuum. The a-Si films were deposited onto sapphire substrates with Cr electrodes 0·5 mm apart in gap configuration. The substrates could be heated up to 500°C. After preparation the samples were transferred to a computerized evacuated measuring device and annealed for 90 min with stepwise increasing temperatures. Immediately after this the temperature dependence of the electrical conductivity was measured using cooling rates of about 4 K min^{-1}.

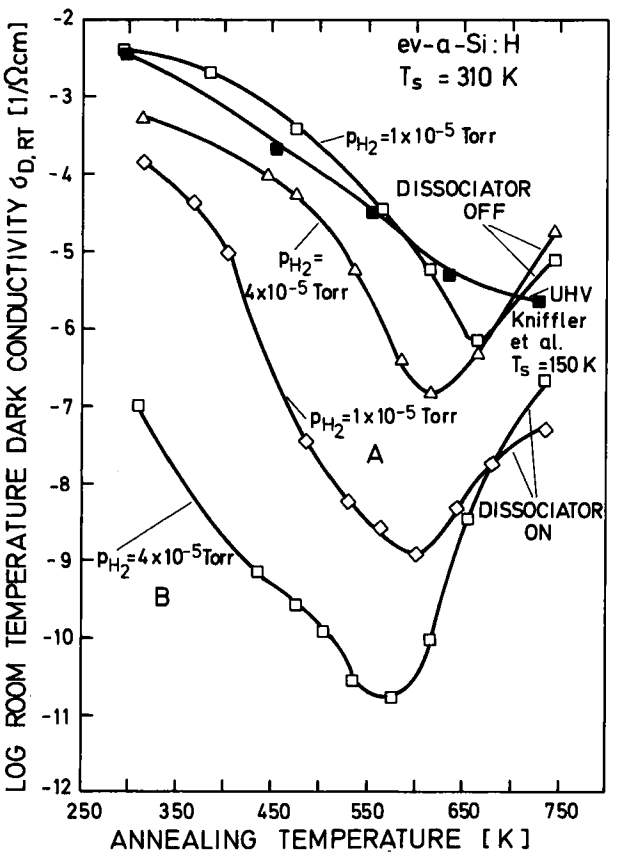
For photoconductivity measurements, the samples were illuminated with a He–Ne laser ($\lambda = 632$ nm, 0·6 mW cm^{-2} or $1{\cdot}8 \times 10^{15}$ photons $cm^{-2}\ s^{-1}$).

§ 3. Results of the hydrogenation procedure

3.1. *Substrate at room-temperature*

Ghosh, McMahon, Rock and Wiesmann (1979) found that molecular hydrogen is unable to passivate the electrically active defects. We have similarly prepared several samples at room temperature in an atmosphere of molecular hydrogen, after which the films were treated by an annealing procedure. The dark conductivity was found to decrease with increasing annealing temperature T_A from $10^{-4}\ \Omega^{-1}\ cm^{-1}$ to a minimum value of about $10^{-7}\ \Omega^{-1}\ cm^{-1}$ (fig. 1).

Fig. 1



Room-temperature dark conductivity of amorphous silicon films evaporated in ultra-high vacuum (Kniffler *et al.* 1981) and in a hydrogen atmosphere for two partial pressures with and without dissociation after annealing to various temperatures T_A. T_S is the substrate temperature during deposition.

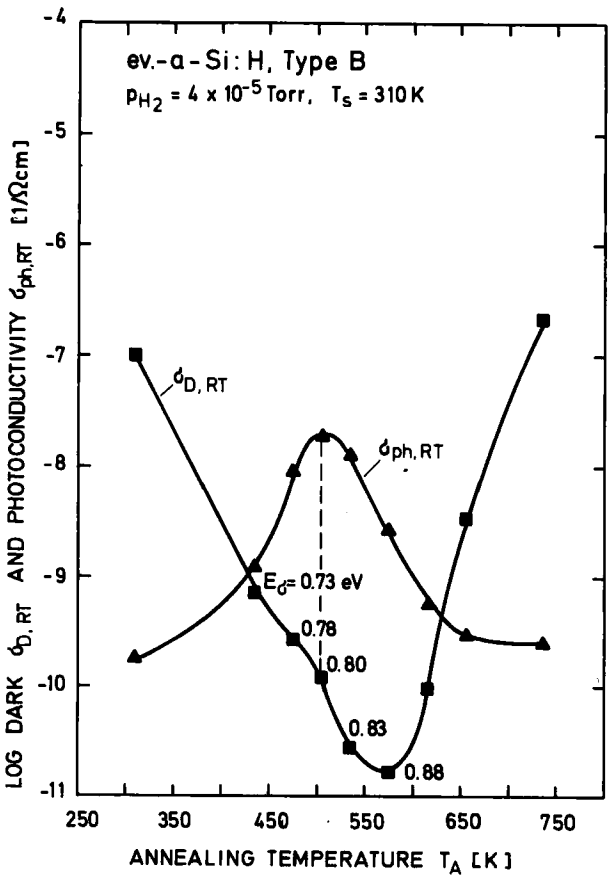
Electrical conduction by hopping near the Fermi level was observed. It should be mentioned incidentally that all gauges in the evaporation vacuum chamber had to be switched off, since the hot cathode of, for example, the quadrupole mass spectrometer had a noticeable influence on the electrical properties of the sample. Many films of this kind were mechanically rather

unstable and peeled off from the substrate, indicating internal stress. The photoconductivity of these films was below $10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature. Figure 1 also shows for comparison the room-temperature conductivity of a pure a-Si film prepared in UHV (Kniffler *et al.* 1981).

As soon as the dissociator was switched on, the electrical properties of the samples changed considerably. The room-temperature dark conductivity immediately after preparation was lower than before, and the minimum value of the conductivity obtained by the thermal treatment was much lower. Figure 1 illustrates the annealing behaviour for the hydrogen pressures $p_{H_2} = 10^{-5}$ Torr (sample A) and 4×10^{-5} Torr (sample B). We find for sample A a minimum dark conductivity of $\sigma_{D,RT} = 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at $T_A = 610$ K, and for sample B an even lower minimum conductivity, $\sigma_{D,RT} = 10^{-11}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at $T_A = 565$ K. Beyond these annealing temperatures, the room-temperature dark conductivity increased again.

Figure 2 shows the annealing behaviour of sample B again, together with the photoconductivity. The photoconductivity of this film first increases with

Fig. 2



Dark conductivity and photoconductivity at room temperature as a function of annealing temperature T_A. Where values for the activation energy E_σ are given, the dark conductivity is activated at room temperature.

annealing temperature T_A by two orders of magnitude, and then drops nearly to its initial value. It is worth mentioning that the maximum in the photoconductivity does not coincide with the minimum in the dark conductivity, although it might seem reasonable to assume that the minimum defect density occurs at this annealing temperature.

The behaviour of the photoconductivity may be explained by following the arguments put forward by Anderson and Spear (1977). At the lowest and highest annealing temperatures the dark conductivity and the photoconductivity are produced by hopping, which is made possible by the large defect density within the gap. In these cases the photoconductivity is nearly independent of the actual density of defects (Voget-Grothe, Kümmerle, Fischer and Stuke 1980). We assume the gap defects to be a combination of donor-like defects extending from the valence band and acceptor-like defects extending from the conduction band. With increasing annealing temperature, the defect density decreases and the hopping conductivity falls ; the number of positively charged defects above the Fermi level, however, is still large, and their charge cloud acts on the electrons predominantly carrying the photoconductivity as a recombination centre with a large cross-section. With decreasing defect density this charge diminishes and the photoconductivity increases. If the annealing process is continued further, the gap defect density becomes so low that the position of the Fermi level responds sensitively. The donor-like defects are occupied more quickly than the acceptor-like defects, and the Fermi level is shifted towards the valence band. In contrast, it is observed experimentally that the distance between the Fermi level and the mobility edge of the conduction band increases. This increase can also be caused by the mobility edge moving up. Either way a positive charge distribution develops above the Fermi level, and depresses the photoconductivity like weak boron doping. It should be mentioned that some films with a low photoconductivity show a second maximum near $T_A = 700$ K.

In the annealing behaviour of the dark conductivity (fig. 2), a shoulder was found around $T_A = 500$ K which is quite similar to that found by Voget-Grothe *et al.* (1980) in the annealing behaviour of the spin density of gd-a-Si : H films after bombardment with energetic electrons. These authors explained this shoulder as being caused by the formation of T_2^0 defects after the effusion of atomic hydrogen from a SiH_2 site. This would agree with the temperature dependence of the infrared absorption of the SiH_2 mode at 2100 cm^{-1} as measured by Kniffler, Schröder and Geiger (1983).

For annealing stages up to 610 K, the films of type B gave the following results : charge transport was activated with a single activation energy over the entire temperature range, and there was no kink in a plot of log σ_D against $1/T$. At higher annealing temperatures T_A, hopping was observed to be the dominant transport mechanism at room temperature. With increasing annealing temperature, the onset of activated conduction takes place at progressively higher temperatures.

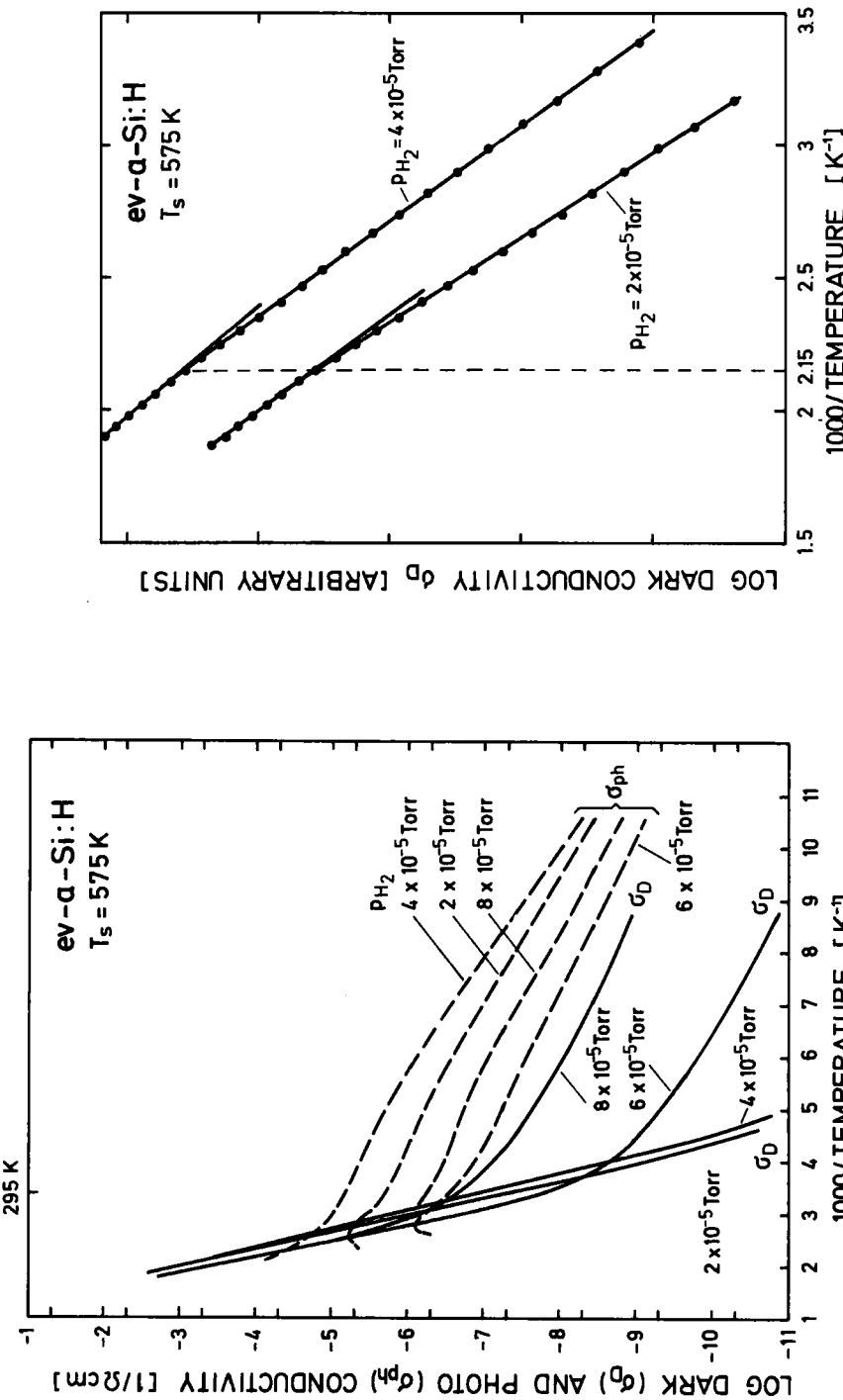


Fig. 3

(*a*) Temperature dependence of the dark conductivity and the photoconductivity of a-Si with hydrogen partial pressure p_{H_2} as a parameter; $T_s = 575$ K. (*b*) Enlarged detail from (*a*) near the kink.

3.2. *Elevated substrate temperatures*

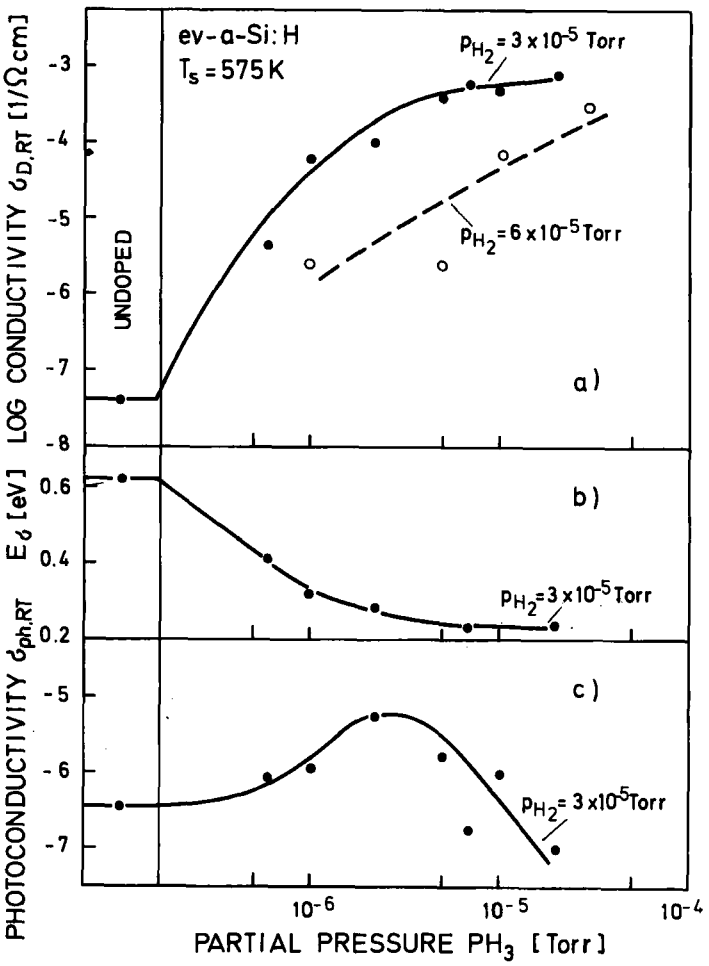
Past experience of preparing a-Si films by glow-discharge deposition or by sputtering has shown that substrate temperatures higher than room temperature are necessary in order to produce samples with satisfactory photoelectric properties. If the substrate temperature is raised and other conditions are kept constant, the room-temperature dark conductivity at the annealing minimum increases and the minimum is shifted to a higher annealing temperature. Obviously, at higher substrate temperatures less hydrogen is incorporated into the film and the defect passivation is less effective ; the same behaviour has already been observed by Dellafera, Labusch and Roscher (1982). Therefore ev-a-Si films were prepared at $T_S = 575$ K and various H_2 partial pressures. The temperature dependence of the dark electrical conductivity for temperatures below the substrate temperature T_S of these films are presented in fig. 3. For hydrogen partial pressures of 2×10^{-5} and 4×10^{-5} Torr the dark conductivity is activated over the entire range measured. At higher pressures, hopping becomes the dominant transport mechanism at room temperature. Figure 3 (*b*) shows that all these evaporated a-Si : H films exhibit a distinct kink near 465 K (see also Spear, Allan, Le Comber and Ghaith 1980).

The photoconductivity of the same samples is also shown in fig. 3. For the ev-a-Si film with a dark conductivity activation energy E_σ around 0·6 eV, a room-temperature photoconductivity higher than $10^{-6}\ \Omega^{-1}\ cm^{-1}$ is obtained. In order to compare the photoconductivity obtained in the present work with the results of other authors, the product $\eta\mu\tau$ was calculated. For an evaporated a-Si : H film with $T_S = 575$ K and $p_{H_2} = 3 \times 10^{-5}$ Torr, $\eta\mu\tau = 2{\cdot}5 \times 10^{-7}\ cm^2\ V^{-1}$ at $E_\sigma = 0{\cdot}63$ eV. The best value obtained for P-doped ev-a-Si : H is $\eta\mu\tau = 4 \times 10^{-6}\ cm^2\ V^{-1}$ at $E_\sigma = 0{\cdot}55$ eV. The former value has to be compared with $\eta\mu\tau \cong 10^{-5}\ cm^2\ V^{-1}$ at $E_\sigma = 0{\cdot}64$ eV for gd-a-Si : H (Anderson and Spear 1977) and $\eta\mu\tau = 1{\cdot}5 \times 10^{-5}\ cm^2\ V^{-1}$ at $E_\sigma = 0{\cdot}63$ eV for sputtered a-Si : H (Turner, Thomas, Allison, Thompson, Rhodes, Austin and Searle 1981). Non-hydrogenated evaporated a-Si films with hopping conductivity gave values of $\eta\mu\tau$ of the order of $10^{-11}\ cm^2\ V^{-1}$.

§ 4. Doping of evaporated films

Several attempts to dope evaporated amorphous silicon films by Li, Na, K, F, Sb, Ni and B, either by implantation, subsequent indiffusion or co-evaporation, are known from the literature (Beyer, Barna and Wagner 1979, Beyer, Stritzker and Wagner 1980, Jang, *et al.* 1980, Beyer 1979, Schubert, Fang and Kinnier 1981). In the present paper it will be shown that the electrical properties of evaporated a Si : H films can be controlled, like gd-a-Si : H or sp-a-Si : H, by the addition of phosphine to the hydrogen atmosphere during the evaporation process. Figures 4 (*a*), 4 (*b*) and 4 (*c*) show respectively the changes in the room-temperature dark conductivity, the activation energy $E_\sigma = E_c - E_F$ and the room-temperature photoconductivity with the phosphine partial pressure for two different H_2 partial pressures. From fig. 4 it is obvious that a phosphine partial pressure of some 10^{-7} Torr is sufficient to alter the electrical properties of the film decisively ; for example, the room-temperature dark conductivity increases by two or three orders of

Fig. 4



(*a*) Room-temperature dark conductivity of evaporated amorphous phosphorous-doped silicon films, (*b*) the activation energy E_σ and (*c*) the photoconductivity at room temperature.

magnitude. Thus the evaporated film reacts very sensitively to the admixed doping gas. The dark conductivity increases rapidly to $\sigma_{D,RT} = 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ if the H_2 partial pressure is held at $p_{H_2} = 3 \times 10^{-5}$ Torr ; for $p_{H_2} = 6 \times 10^{-5}$ Torr this increase is much slower. This behaviour can be understood from the results for undoped films, because for the higher hydrogen partial pressure the dark conductivity is no longer activated, and in addition the dissociated phosphine may increase the amount of atomic hydrogen even more. Therefore, the H_2 partial pressure suitable for undoped ev-a-Si : H films exceeds the optimum value with increasing doping pressure. It is interesting to note that even films which do not show activated conductivity over the entire temperature range can still be doped quite efficiently.

As the room-temperature dark conductivity increases, the activation energy E_σ decreases and reaches almost $E_\sigma = 0{\cdot}2$ eV at the conductivity maximum. The photoconductivity increases first with increasing phosphine partial pressure and then drops again. Presumably, PH_x molecules are incorporated as the film grows because of incomplete dissociation of the phosphine molecules, higher numbers of which reduce the photoconductivity by acting as a structural defect.

Acknowledgments

The support of this work by the Bundesministerium für Forschung und Technologie is gratefully acknowledged. Thanks are due to J. Pirrung and W. Müller for useful discussions and technical assistance.

References

Anderson, D. A., and Spear, W. E., 1977, *Phil. Mag.* B, **36**, 695.
Beyer, W., 1979, *Solid St. Commun.*, **29**, 291.
Beyer, W., Barna, A., and Wagner, H., 1979, *Appl. Phys. Lett.*, **35**, 539.
Beyer, W., Stritzker, B., and Wagner, H., 1980, *J. non-crystalline Solids*, **35–36**, 321.
Beyer, W., and Stuke, J., 1975, *Phys. Stat. Sol.* (a), **30**, K155.
Brodsky, M. H., Title, R. S., Weiser, K., and Petit, G. D., 1970, *Phys. Rev.* B, **1**, 632.
Dellafera, P., Labusch, R., and Roscher, H. H., 1982, *Phil. Mag.* B, **45**, 607.
Fischer, J. E., and Donovan, T. M., 1972, *J. non-crystalline Solids*, **8–10**, 202.
Ghosh, A. K., McMahon, T., Rock, E., and Wiesmann, H., 1979, *J. appl. Phys.*, **50**, 3407.
Grigorovici, R., Croitoru, N., and Devenyi, A., 1967, *Phys. Stat. Sol.*, **23**, 621.
Jang, J., Kang, J. H., and Lee, C., 1980, *J. non-crystalline Solids*, **35–36**, 313.
Kaplan, D., Sol, N., Velasco, G., and Thomas, P. A., 1978, *Appl. Phys. Lett.*, **33**, 440.
Kniffler, N., Müller, W., Pirrung, J., Hänisch, N., Schröder, B., and Geiger, J., 1981, *J. Phys, Paris, Suppl.*, **42**, C4, 811.
Kniffler, N., Schröder, B., and Geiger, J., 1983, *J. non-crystalline Solids*, **58** (in the press).
Lewis, A., 1972, *Phys. Rev. Lett.*, **29**, 1555.
Malhotra, A. K., and Neudeck, G. W., 1976, *Appl. Phys. Lett.*, **28**, 47.
Miller, D. L., Lutz, H., Wiesmann, H., Rock, E., Ghosh, A. K., Ramamoorthy, S., and Strongin, M., 1978, *J. appl. Phys.*, **49**, 6192.
Paul, W., Lewis, A. J., Connell, G. A. N., and Moustakas, T. D., 1976, *Solid St. Commun.*, **20**, 969.
Schubert, C. C., Fang, P. H., and Kinnier, J. H., 1981, *Japan J. appl. Phys.*, **20**, L437.
Spear, W. E., 1977, *Adv. Phys.*, **26**, 811.
Spear, W. E., Allan, D., Le Comber, P., and Ghaith, A., 1980, *Phil. Mag.* B, **41**, 419.
Spear, W. E., and Le Comber, P. G., 1975, *Solid St. Commun.*, **17**, 1193; 1976, *Photoconductivity and related phenomena*, edited by J. Mort and D. M. Pai (New York: Elsevier), p. 185.
Turner, D. P., Thomas, I. P., Allison, J., Thompson, M. J., Rhodes, A. J., Austin, I. G., and Searle, T. M., 1981, *Tetrahedrally bonded Amorphous Semiconductors* edited by R. A. Street, D. K. Biegelsen and J. C. Knights, A.I.P. Conf. Proc. No. 73 (New York: American Institute of Physics), p. 47.
Voget-Grothe, U., Kümmerle, W., Fischer, R., and Stuke, J., 1980, *Phil. Mag.* B, **41**, 127.