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Thermally induced metastability and the Meyer–Neldel rule in hydrogenated amorphous silicon

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Abstract. A stepwise decrease in the annealing temperature alters the conductivity prefactor σ_0 and activation energy E_A of a-Si:H and a linear dependence of ln σ_0 on E_A occurs (the Meyer–Neldel rule). It is assumed that temperature-induced changes in the density of states in the mobility gap are responsible for this behaviour. Furthermore, these results are compared with the influence of a stepwise annealing of light-induced defects on temperature-dependent conductivity. The experimental findings are evidence for the existence of a generalised Meyer–Neldel rule in a-Si:H.

1. Introduction

Thermally activated conductivity via extended states in hydrogenated amorphous silicon (a-Si:H) can be described experimentally by the Arrhenius equation

$$\sigma(T) = \sigma_0 \exp(-E_A/kT). \tag{1}$$

Assuming that the positions of the conduction band mobility edge $E_C(T)$ and the Fermi level $E_F(T)$ are both linear functions in the temperature range treated (Overhof and Beyer 1981), we obtain the activation energy E_A as the difference between the linear extrapolations of $E_C(T)$ and $E_F(T)$ to zero temperature, and the conductivity prefactor σ_0 is determined by the linear shift coefficients.

The existence of a relationship between the conductivity prefactor and activation energy of doped and undoped a-Si:H was first reported by Rehm *et al* (1977), Carlson and Wronski (1979) and Spear *et al* (1980). Fritzsche (1980) named this relation the Meyer–Neldel rule (MNR):

$$\sigma_0 = \sigma_{00} \exp(GE_A) \tag{2}$$

where σ_{00} and G are the MNR prefactor and the MNR slope, respectively. Under the assumption that the statistical shift of $E_F(T)$ is the reason for the MNR the slope G describes the dependence of the linear shift coefficient $\Gamma_F(E_F)$ which is determined by the density-of-states (DOS) distribution within the mobility gap (Overhof and Beyer 1981, Druesedau *et al* 1987) (a complete discussion has been given by Overhof and Thomas (1988)). In recent work, Druesedau and Bindemann (1986) referred to the existence of a regular relationship between σ_{00} and G which was named the generalised MNR in a-Si:H.

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Irsigler *et al* (1983) have shown that stepwise annealing of light-induced defects in a-Si: H also causes MNR behaviour of the $\sigma_0(E_A)$ curves. This experiment was simulated by a systematical change in the DOS in the mobility gap and numerical calculations of the statistical Fermi level shift $E_F(T)$, proving additionally the existence of a generalised MNR (Druesedau *et al* 1987).

Recently an increasing number of papers (Smith *et al* 1986, Street *et al* 1987, Meaudre *et al* 1988) have reported studies on thermally created metastable defects. It was shown that variations in thermal treatment, e.g. altered annealing temperature or annealing time, change the value of the activation energy E_A of thermally activated conductivity $\sigma(T)$ (Toth *et al* 1987). The aim of this paper is to investigate the influence of the annealing temperature on σ_0 and E_A. Further, the experiment proposed by Irsigler *et al* (1983) was applied to some chosen samples in comparison with previous experiments.

2. Experimental details and results

The annealing experiment was carried out as follows. Samples were annealed at 453 K for 1 h and cooled to 433 K; measurements of the DC conductivity were then performed. Next the samples were kept at 433 K for 1 h, and conductivity measurements were then performed between 433 and 413 K, etc. The temperatures for the 1 h anneal were chosen to be 453, 433, 413, . . . , 333 K.

The samples investigated were highly photosensitive a-Si: H and a-SiN_x: H films (photo-to-dark-conductivity ratio $\sigma_F/\sigma_D = 3 \times 10^5$ at maximum) prepared by DC magnetron sputtering (Druesedau *et al* 1989) and a-Si: H films deposited by sputter-assisted plasma-enhanced chemical vapour deposition (SAPCVD) (Kottwitz *et al* 1987). The thicknesses of films were in the range 400–600 nm. The measurements were performed in a coplanar electrode arrangement with evaporated Al electrodes of 1 mm interelectrode spacing and an electric field E of 1000 V cm^{-1} under vacuum conditions (pressure below 10^{-1} Pa).

Typical results from the experiment described above are shown in figure 1. One can see that each annealing process effects a gradation of the $\sigma(T)$ curve. The incorporation of nitrogen into a-Si: H increases this effect.

Figure 2 presents the dependence of the prefactor σ_0 on the activation energy E_A measured for a-Si: H and a-SiN_x: H films. The experimental uncertainty calculated from the linear fit of ln σ versus $1/T$ was always below 1% for the activation energy and below 3% for the prefactor. Hence the observed changes in both quantities due to thermal treatment are a real measured effect. The MNR is valid for each sample. Some films follow the MNR with two parameter pairs σ_{00} and G. The kink behaviour (curves A, C and D) is also observed in light-induced changes of $\sigma(T)$ (see, e.g., Irsigler *et al* 1983). Previous investigations (keeping the films for 1 h at 373 K and subsequent cooling) agree with the present results. The repetition of the annealing experiment (100 d later) gives evidence of the good reproducibility of these data.

The experiment proposed by Irsigler *et al* (1983) was applied in a modified form (illumination for 1 h at room temperature; stepwise annealing at T_A = 333, 353, . . . , 453 K) to some chosen samples. Figure 3 displays the result of this procedure as a plot of ln σ_0 versus E_A in comparison with the influence of only the thermal treatment. It is evident that the MNR parameters of both procedures differ from each other. Further, the dependence of σ_0 and E_A on annealing temperature is non-monotonic for the experiment of Irsigler *et al* and becomes inverse between 393 and 413 K.

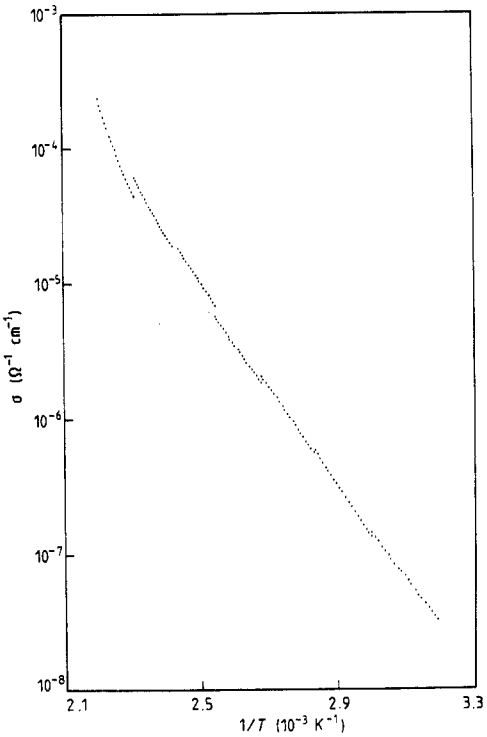

Figure 1. Temperature dependence of DC dark conductivity σ of a stepwise annealed a-SiN_x:H film.

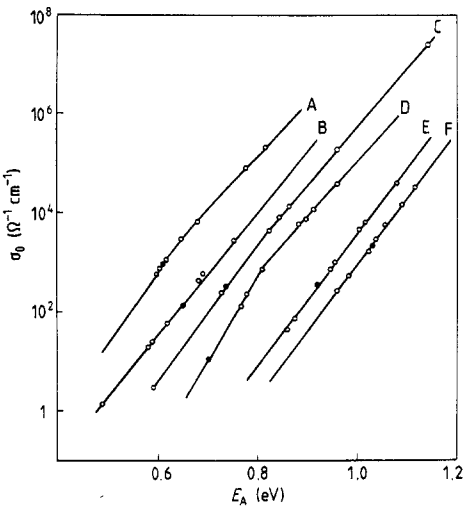

Figure 2. Conductivity prefactor σ_0 as a function of activation energy E_A measured for stepwise annealed SAPCVD a-Si:H (curve A), sputtered a-Si:H (curve D) and a-SiN_x:H (curves B, C, E and F). The full symbols are for σ_0 and E_A obtained after annealing for 1 h at 373 K and cooling to 313 K.

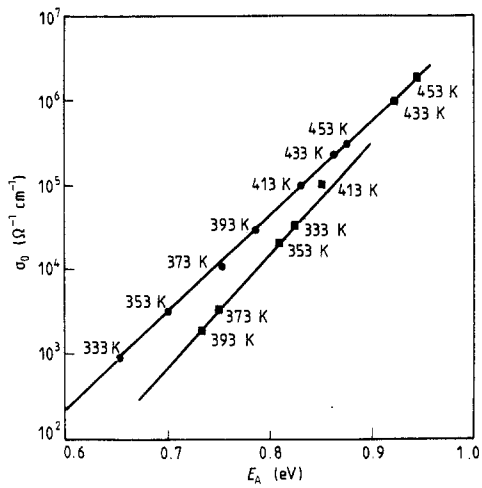

Figure 3. Dependence of the conductivity prefactor σ_0 on the activation energy E_A for an a-Si:H sample measured after annealing experiment (●) and for stepwise annealing of light-induced defects (■).

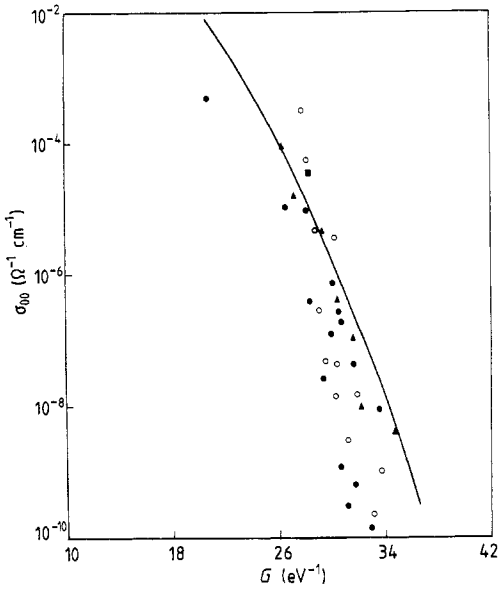

Figure 4. Parameters of the MNR obtained from various samples: ○, a-Si:H films prepared by DC magnetron sputtering; ●, a-SiN_x:H films prepared by DC magnetron sputtering; ▲, a-Si:H films prepared by SAPCVD; ■, unhydrogenated a-Si film; ——, square approximation to experimental $\sigma_{00}(G)$ data in figure 1 of Druesedau and Bindemann (1986).

Figure 4 displays all pairs of MNR parameters σ_{00} and G derived from the thermal treatment of a variety of samples and gives further evidence for the existence of a generalised MNR in a-Si:H, which agrees with data from other laboratories.

3. Discussion

In previous work (Smith *et al* 1986, Street *et al* 1987, Branz *et al* 1987, Redfield 1988, Redfield and Bube 1989) it was shown that thermal defect creation is very common in the Staebler-Wronski effect (SWE) which is known to be a true bulk effect (Stutzmann *et al* 1985). The influence of the SWE on the thermally activated conductivity measured under conditions very similar to those of the present work (Irsigler *et al* 1983) was found to be in good agreement with model calculations based on changes in the DOS (Druesedau *et al* 1987). Hence, as in the present work changes in activation energy and prefactor in a similar manner to the experiment of Irsigler *et al* were observed, one is forced to assume that changes in the DOS are responsible for this behaviour and the effect should result from the bulk of the film rather than from its surface. Another argument for the bulk nature of the observed effect arises from the comparison of a-Si:H and a-SiN_x:H ($x < 0.1$) films which were prepared under identical conditions (except for the nitrogen partial pressure) and therefore had the same optical gap and room-temperature conductivity (Druesedau *et al* 1989). Nitrogen-containing films exhibit much stronger changes in activation energy and prefactor than nitrogen-free films.

The basic idea for drawing conclusions about the variations in the DOS is the same as was used to explain the influence of annealing of light-induced defects on conductivity (Druesedau *et al* 1987). At a fixed temperature an increase in the DOS will always shift the Fermi level to lower energies and vice versa; the decreasing DOS causes the Fermi level to move to higher energies.

Hence the result presented in figure 1 can be explained as follows. Annealing at higher temperatures causes thermal equilibrium to be reached quickly; this is concluded from the experimental data of Meaudre *et al* (1988). Therefore, these metastable states have a much longer time for stabilisation and the DOS is weakly changed during the phase obtained immediately after cooling. So, the next isothermal treatment causes a remarkable alteration in conductivity at this temperature. The time necessary to reach thermal equilibrium increases at lower annealing temperatures, and then thermal equilibrium is not reached during the 1 h isothermal treatment but relaxations of the DOS occur during the cooling phase too. From the results of Smith *et al* (1986) it is evident that cooling rates of 1 K min^{-1} are slow enough to permit relaxations of the DOS. The decrease in the DOS with decreasing temperature shifts the Fermi level upwards and hence contributes a negative component to the shift coefficient Γ_F. This negative component is superposed on the component due to the statistical shift, resulting in smaller values at low temperatures where DOS relaxation occurs during the cooling phase. Therefore, from the definitions of σ_0 and E_A given by Beyer and Overhof (1984),

$$\begin{aligned} \sigma_0 &= \sigma_M \exp[(\Gamma_C + \Gamma_F)/k] \\ E_A &= E_{C^+} - E_{F^+} \end{aligned} \tag{3}$$

where σ_M is Mott's fundamental prefactor (Overhof and Thomas 1988), Γ_C is the shift coefficient of the conduction band mobility edge, E_{C^+} and E_{F^+} are the linear extrapolations of $E_C(T)$ and $E_F(T)$, respectively, to zero temperature, one should expect smaller values of σ_0 and E_A at lower temperatures, which is indeed observed (see figure 3). With respect to the reproducibility of σ_{00}- and G-values one can conclude that the MNR parameters are typical for the changes in the DOS of each sample.

Further, irradiation with light and thermal treatment are of different influence on the DOS as is evident from figure 3. The effect of stepwise annealing of light-induced defects on σ_0 and E_A up to about 400 K is in agreement with model calculations (Druesedau *et al* 1987) and results from the reduction in defect states due to annealing. At higher temperatures the process of thermal defect creation becomes dominant and the values of σ_0 and E_A are similar to those of the annealing experiment. In previous work (Irsigler *et al* 1983) such behaviour for undoped and n-doped glow-discharge a-Si:H was not found. Obviously our experiment is a confirmation of recent work by Meaudre *et al* (1988) which might prove a lower equilibrium temperature for sputtered a-Si:H.

The pairs of MNR parameters (see figure 4) obtained for all films investigated are direct experimental evidence for the existence of the generalised MNR in a-Si:H. In particular, films prepared by SAPCVD obey well the regular relationship between σ_{00} and G which was found from experimental data (Druesedau and Bindemann 1986).

4. Conclusions

The investigations show that the activation energy of thermally activated conductivity above room temperature is not a well defined measure for characterisation of a-Si, because it is always influenced by treatment before and during measurements. In contrast with this the value of G is not changed by thermal treatment and hence is typical for each sample.

Probably, measurements of $\sigma(T)$ behaviour can be unique only at very slow cooling rates, because the results are then obtained near the thermal equilibrium.

Finally the validity of the generalised MNR for all a-Si-based samples investigated independent of the kind of energetic stimulation (light or thermal energy) is obvious founded on a material constant—the fundamental pre-exponential factor σ_M.

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