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ELECTRONIC PROPERTIES OF MICROCRYSTALLINE SILICON FILMS PREPARED IN A GLOW DISCHARGE PLASMA

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Abstract. The properties of glow discharge microcrystalline Si have been investigated by conductivity, Hall effect and field effect measurements as a function of crystallite size and phosphorus doping ratio. It is concluded that the large increase in $\sigma$ over a-Si is almost entirely caused by an increased carrier density resulting from delocalised electron tail states. The sign of the Hall constant remains normal down to an extrapolated crystallite size of about 20Å.

1. Introduction.

The work of Vepr'ek and his collaborators (1) has shown that by chemical transport in a hydrogen glow discharge plasma, microcrystalline (μc) layers of Si can be deposited at a substrate temperature as low as $80^\circ$C. The Zürich group suggested that under conditions whereby a chemical equilibrium is established at the plasma-solid interface, stable nuclei are likely to be formed, leading to microcrystalline growth. Recently work in other laboratories (2)(3)(4) has shown that μc films can also be deposited from the silane glow discharge, widely used in the preparation of a-Si specimens. Chemical equilibrium in this case is approached by strong hydrogen dilution. The possibility of controllable μc plasma deposition could be of considerable applied interest; it also permits an extension of fundamental studies on the electronic properties just beyond the a-phase as a function of structural ordering. In the following we should like to report some of our recent work in this direction.

2. Preparation and Structural Measurements.

Specimens were prepared at a substrate temperature of $280^\circ$C in a capacitatively coupled deposition unit. The gas mixture consisted of 3% (or 2% in some cases) of silane in hydrogen with the required addition of phosphine in the case of the doped specimens. In the light of Vepr'ek's interpretation, the strong dilution of the silane by hydrogen enhances the reverse reaction (erosion) at the growing interface and moves the reaction closer towards equilibrium. The resulting decrease in the deposition rate has been partly compensated by using a somewhat higher R.F. power of 18-25 W. This led to a deposition rate of about 0.1Å s$^{-1}$.

The average crystallite size $\delta$ was determined for each deposition run from the half-width of the (111) electron diffraction ring by means of the Scherrer formula. The use of electron diffraction in this connection was checked by X-ray measurements. The results show that crystallite sizes in the range from about 18Å to 60Å can be obtained from the glow discharge. $\delta$ depends critically on plasma conditions, the amount of hydrogen dilution and, somewhat unexpectedly, on the excitation frequency. Of the 20 glow discharge microcrystalline (gd-μc) specimens so far studied, most of the larger crystallite sizes were produced at the highest frequency of 40 MHz.

The properties of thermally crystallised (th-μc) glow discharge specimens have been investigated in previous work (5). For comparison we have included some measurements on such specimens crystallised at $800^\circ$C. Their crystallite sizes lie above those of the gd-μc samples, generally between 60Å and 100Å. On the other end of the scale, the electron diffraction line width of typical a-Si specimens places them at a nominal $\delta$ between 10 and 12Å on the Scherrer correlation graph. This is merely an extrapolation and no physical significance should be attached to this result.
The electron diffraction pictures in figs.1a,b,c demonstrate very clearly the difference between the \(a\)- and the \(gd\)-\(\mu\)-phases. (a) and (b) compare the results from an \(a\)-\(Si\) and a \(gd\)-\(\mu\) specimen (\(\delta = 50\)A) taken in the microdiffraction mode in a STEM. (b) is a (110) pattern from a single microcrystallite and its twin orientation. However, for the determination of \(\delta\) a high resolution diffraction stage was used in which a large number of crystallites (over an area measuring about 60 \(\mu\)m) contribute to the ring pattern shown in (c), obtained for the same specimen as in (b).

**Fig.1.** Electron diffraction results. (a) \(a\)-\(Si\), (b) and (c) \(gd\)-\(\mu\) (\(\delta = 50\)A).

### 3. Conductivity.

Fig.2 summarises the room temperature conductivity \(\sigma_{RT}\) as a function of the doping ratio for \(a\)-\(Si\), \(gd\)-\(\mu\)-\(Si\) and \(th\)-\(\mu\)-\(Si\). Results for several undoped specimens (U) have also been included. It can be seen that the conductivity of the \(gd\)-\(\mu\) specimens is over two orders of magnitude higher than that of the doped \(a\)-\(Si\) and reaches 200(\(\text{cm}^{-1}\)) at the highest doping level. All the results refer to specimens deposited at 40 MHz. The spread in the experimental points is caused mainly by different crystallite sizes which, as we shall see in the next section, are a determining factor in the carrier mobility. The solid line refers to \(\delta = 50\)A, and some of the lower crystallite sizes are given in fig.2. Thermally crystallised specimens lead to \(\sigma_{RT}\) values at least an order of magnitude higher than those crystallised in the glow discharge. The \(\mu\) specimens show a conductivity activation energy which is the sum of \(\varepsilon_n\) and \(\varepsilon_H\), the activation energies associated with carrier density and Hall mobility. These will be discussed in the next section.

**Fig.2.** Room temperature conductivity plotted against doping ratio for \(a\)-\(Si\), \(gd\)-\(\mu\) and \(th\)-\(\mu\) \(Si\). U denotes undoped specimens.

### 4. Hall Effect.

Extensive Hall effect measurements have been carried out on the \(\mu\) specimens between 440K and 210K, using the technique described previously in measurements on \(a\)-\(Si\) (6). The Hall effect in polycrystalline semiconductors has received a considerable amount of attention in the literature and is reviewed in a recent article by Orton and Powell (7). The interpretation depends to some extent on the structural model assumed for the material. As we know little about the structural details, we shall regard the electron density \(n\), and electron mobility \(\mu_H\), as approximate average values over the \(\mu\) specimen.

#### 4.1 Carrier density.

Fig.3 shows the dependence of the room temperature carrier density on the gaseous doping ratio \(PH_3/SiH_4\) expressed in vppm (see top scale) for both \(gd\)-\(\mu\) and
Fig. 3. Carrier density (20°C) for gd-uc specimens plotted against donor density (ND) estimated from the gas phase.

Fig. 4. Activation energy $E_a$ plotted against n.

Th-uc samples. The lower scale in fig. 3 gives corresponding donor densities $(N_D)_G$, calculated on the assumption that the gaseous doping ratio is maintained in the solid. The results show clearly that carrier densities obtained for a given doping ratio are independent of the method of crystallisation and of the grain size. The line $N_D = 0.5(N_D)_G$ gives an approximate fit over several orders of magnitude. In agreement with previous results (8) we therefore suggest that about half the phosphine molecules in the plasma introduce a P-site into the solid, most of which act as donors in the uc phase. (5). At the highest $N_D$, points tend to lie consistently below this line; the effect arises most probably from the movement of $\epsilon_f$ into the donor band, so that $N_f/N_D < 1$.

In fig. 4 the measured activation energy $E_a$, associated with the carrier density, has been plotted against $n$. We believe that the initial decrease of $E_a = \epsilon_f - \epsilon_f$ for $n < 10^{18} \text{cm}^{-3}$ reflects the movement of $\epsilon_f$ into the donor band, but that the subsequent part of the curve shows mainly the decrease in the donor ionisation energy (9). The latter vanishes at $N_D = 5 \times 10^{19} \text{cm}^{-3}$.

4.2 Hall Mobility.

Room temperature $\mu_H$ values for the gd-uc specimens generally lie below $1 \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$, and are largely independent of the doping level. However, the correlation in fig. 5 shows that $\mu_H$ decreases with decreasing $\delta$. The Hall coefficient in gd-ucSi is negative, the expected sign for electron transport on the macroscopic theory. $\mu_H$ extrapolates to zero at a critical grain size of about 20A and the line then passes through the Hall mobility measured in a-Si with anomalous sign (6) at the nominal $\delta = 12$A. This result is of considerable interest; it provides the limiting size of the ordered regions in this material for which the classical approach to the Hall effect is applicable. At $\delta < 20$A the microscopic interpretation discussed by Friedman (10) and Emin (11) become relevant.

The temperature dependence of $\mu_H$ is found to be of the form:

$$\mu_H = \mu_0 \exp(-\epsilon_f/kT).$$

$\epsilon_f$, which for the gd-uc specimens lies between 40 and 100 meV, has often been interpreted as a measure of the average barrier height between crystallites (7). $\mu_0$ is a measure of the Hall mobility in the crystallite having an average size $\delta$. It lies between 1 and 10 $\text{cm}^2\text{V}^{-1}\text{sec}^{-1}$ and, like $\mu_H$, depends on $\delta$. $\mu_0$ values are therefore quite comparable to extended state mobilities in a-Si, deduced from drift mobility experiments (12). This suggests that the formation of the small
crystalline regions discussed here does not greatly change the transport properties as compared to the $a$-phase.

Finally, Hall effect measurements on th-$\mu$C specimens lead to $\mu_{H}$ values about ten times higher than those for $gd$-$\mu$C samples. The difference between the two $\partial/\partial T$ curves in fig.2 is therefore entirely accounted for by the difference in mobility.

![Fig.5. Hall mobility in gd-$\mu$C specimens plotted against crystallite size.](image)

5. Discussion.

The results of the previous section have established that the increased conductivity observed in the $\mu$C specimens as compared to the $a$-phase is mainly associated with a larger carrier concentration. We should like to suggest that in the $\mu$C phase the increased order is sufficient to delocalise an appreciable range of the tail states. In that case $\varepsilon_{C}$ will now lie close to the donor band and with $(\varepsilon_{C} - \varepsilon_{F})_{o} \approx \varepsilon_{n}$ (see fig.4) the increase in $n$ by two orders of magnitude or more can easily be accounted for. This interpretation is supported by field effect measurements which have been carried out on a number of $n$-type specimens. They indicate that $\varepsilon_{C}$ has been shifted by at least 0.15 eV from its position in $a$-Si, thus delocalising most of the tail states.

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