Amorphous semiconducting Si : H

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Abstract. Glow discharge decomposition of silane produces amorphous semiconductors which can be doped to be either *n*-type or *p*-type. Since these amorphous silicon films contain between 10–20 atomic per cent hydrogen, the density of undesired defects and localized gap states is very low. As a consequence of the high semiconductor quality of the a-Si : H films, space charge layers adjacent to the surface and substrate interface play an important role in the transport properties. We describe the effect of illumination, thermal treatments and surface layers on the conductance and discuss some difficulties in interpreting the field effect in terms of the bulk density of gap states. The preparation and some characteristic properties of the silicon-hydrogen alloys are described.

Keywords. Amorphous silicon; plasma deposition; hydrogen content; conductivity; mobility gap; field effect; infrared absorption; light-induced conductance changes; absorbates; density of states; space charge effects.

1. Introduction

The ability to modify the electronic behaviour of crystalline semiconductors by controlled doping has been essential for their use in solid-state devices and for reaching our present detailed understanding of these materials. For this reason, the discovery by Spear *et al* (1975, 1976) of an amorphous silicon material which can be doped either *n*-type or *p*-type and whose conductivity can be changed by over ten orders of magnitude marked a turning point in the science and technology of amorphous semiconductors. Instead of conventional sputtering or evaporation, they prepared their amorphous silicon films by glow-discharge decomposition of silane (SiH_4). This method, described first by Sterling and Swann (1965), Chittick *et al* (1969), yields a-Si with a very small density of dangling or unsaturated bonds and a correspondingly low density of undesired defect states in the gap. As a consequence one finds a large photoconductivity (Love-land *et al* 1973/1974; Zanzucchi *et al* 1977) and excess carrier life-time (Le Comber and Spear 1970; LeComber *et al* 1972; Wronski 1977; Moore 1977), strong (Engemann and Fischer 1977; Street 1978; Fischer 1979) photoluminescence and electroluminescence (Pankove and Carlson 1976).

It soon became apparent that glow-discharge a-Si owes its remarkable properties to the fact that it contains between 10–20 atomic per cent hydrogen (Triska *et al* 1975; Brodsky *et al* 1977; Fritzsche *et al* 1979) so that it is appropriate to refer to it as a binary alloy, a-Si:H. This alloy has a modified structure without the voids and large number of defects (Connell and Pawlik 1976; Barna *et al* 1977) which limit the usefulness of conventional a-Si. An even superior alloy, a-Si:F:H, can be prepared by using a mixture of SiF_4 and H_2 in the discharge (Ovshinsky and Madan 1978; Ovshinsky 1979; Madan and Ovshinsky 1980). a-Si:H can alternatively be obtained by post-hydrogenation of a-Si (Pankove *et al* 1978; Sol and Kaplan 1980) or by sputtering Si in the presence of hydrogen (Paul *et al* 1976; Lewis 1976; Freeman and Paul 1979).

The field is rapidly expanding with exciting new developments in many directions, and I must refer to recent reviews (Brodsky 1979) and conference proceedings (Spear 1977; Paul and Kastner 1980; Fritzsche 1980) for background information.

It is clear that reliable measurements of the density of states $N(E)$ in the mobility gap and of the basic parameters which characterize the bulk electronic properties of a-Si:H are important for further improvements of this material. In this paper I wish to discuss some difficulties in measuring the bulk properties (Fritzsche 1980). They are related to the fact that one deals with thin films (between 0.5 and 3 μm thick) and that space charge layers adjacent to the surface and substrate interface play an important role in the transport properties when $N(E)$ is small.

I start with a brief description of the plasma deposition system used by us and the determination of the hydrogen content.

2. Glow discharge deposition

Electrons in a plasma possess sufficient energy (~ 10 eV) to break molecular bonds so that chemical reactions can occur at relatively low ambient temperatures. However, the large number of ion fragments in the plasma make the plasma chemistry which governs the growth of the a-Si:H film very complex (Rand 1979) and dependent on a variety of deposition conditions (Knights 1976, 1980). As a consequence films prepared in various laboratories differ considerably. Our system is sketched in figure 1. A gas flow of 10% SiH_4 in Ar at 30 sccm/min is maintained with a pressure of 0.15 Torr by a mechanical forepump. Back diffusion of oil is prevented by a trap between the reaction chamber and the pump. Downstream from the pump the unreacted gas is decomposed in a quartz tube at 800° C passed through water and vented.

The sample substrates are clamped on the 7 cm diameter electrode plates which are separated by 2.5 cm. These plates are connected through a matching circuit to a 13.56 MHz power supply.

The r.f. electrodes acquire a negative d.c. bias relative to the plasma because of the rectification of the r.f. voltage by the plasma. Since the grounded metal surface in contact with the plasma (ground shield and lower electrode), is about twice the area of the upper electrode, the latter has a larger negative potential and is called the cathode. The d.c. potential difference between the anode and cathode plate is typically 90 V for an r.f. voltage of 120 V. The film growth rate

Figure 1. Plasma deposition chamber. Material: stainless steel. F = machinable glass ceramic flange, S = grounded shield, Sc = grounded screen, H = heater-cathode, A = grounded anode.

is close to 1.3 A/sec under these conditions and is essentially the same on the cathode and the anode. For best results both anode and cathode plates are heated to $280 < T_s < 320^\circ \text{C}$.

Doping is achieved by adding PH_3 or B_2H_6 to the SiH_4 at a ratio between 10^{-6} and 10^{-2} . The r.f. power and the gas pressure are kept low and the flow rate relatively high in order to avoid columnar growth (Knights 1980) and pebble-like microstructure (Schiff *et al* 1981) in the films. The occurrence of these can be noticed visually by strong light scattering (cloudiness) and observed in detail by a scanning electron microscope.

Different preparation techniques have been described by various authors (Brodsky 1979); Spear 1977; Paul and Kastner 1980). Nevertheless, the deposition parameters for each system have to be adjusted for optimal results.

3. Hydrogen content

The hydrogen evolution method is simple and inexpensive for determining the hydrogen content (Triska *et al* 1975; Fritzsche *et al* 1978, 1979). About $0.5\text{--}1 \text{ mg}$ of a-Si:H sample is heated in a quartz tube at a rate of approximately 15°C/min until crystallization occurs near 750°C . One either records the pressure increase at constant system volume ($\sim 10 \text{ cm}^3$) or the gas volume increase due to the evolving H_2 gas at constant system pressure. Typical evolution curves using the first method (Fritzsche *et al* 1979) are shown in figure 2. The total hydrogen content is determined from the final reading after letting the sample cool to room temperature. In using this technique we have to assume that essentially no hydrogen is retained in crystallized Si and that there is no out

Figure 2. Hydrogen evolution at heating rate of $15^{\circ}\text{C}/\text{min}$ for samples deposited on the anode A and cathode C. Substrate temperatures ($^{\circ}\text{C}$) are noted in parentheses. A (25)* was deposited at 25°C on the anode while the cathode was heated to 270°C . (After Fritzsche *et al* 1978, 1979).

diffusion of H_2 through the heated tip of the quartz tube. The solubility of H in Si is indeed small. The validity of the second assumption was tested by reheating the tip of the quartz tube for an extended period of time. No significant drop in hydrogen pressure was observed. Mass spectroscopic analysis of the effused gas revealed that the cathode films contain a few per cent of Ar (Tsai and Fritzsche 1979).

Others have determined the H-content by measuring the characteristic 4.43 MeV γ -rays from the nuclear resonant reaction of a beam of $5\text{--}7\text{ MeV}$ nitrogen ions with the hydrogen in the films (Brodsky *et al* 1977a). Similar concentrations were obtained.

Infrared absorption studies reveal that the hydrogen may be bonded in the Si matrix on different sites (Tsai and Fritzsche 1979; Brodsky *et al* 1977 b; Fritzsche 1977; Knights *et al* 1978; Lucovsky *et al* 1979) as a monohydride SiH with a stretching mode at 2000 cm^{-1} , dihydride SiH_2 with a stretching mode near 2100 cm^{-1} and a bending mode at 880 cm^{-1} , trihydride SiH_3 with modes at 2140 , 907 , and 862 cm^{-1} , and $(\text{SiH}_3)_n$ polymers with a stretching mode near 2100 cm^{-1} and bending modes at 845 and 890 cm^{-1} . All of these species have a broad bondrocking absorption at 630 cm^{-1} . Polymeric hydrogen bonding predominates in films deposited near room temperature. Anode films deposited above $T_s = 280^{\circ}\text{C}$ contain SiH almost exclusively.

The effect of the substrate temperature and substrate bias on the relative abundance of various hydride species in a-Si:H is illustrated by figure 3 which shows the stretching mode absorptions of various films (Tsai and Fritzsche 1979). Figure 4

Figure 3. Infrared absorption due to hydrogen stretching modes in anode and cathode films prepared at the temperatures indicated. (After Tsai *et al* 1979).

Figure 4. Area under the stretching mode absorption bands for various films as a function of their total hydrogen content. (After Tsai *et al* 1979.)

shows the area under the stretching mode absorption bands (Tsai and Fritzsche 1979) for various anode and cathode films as a function of the total hydrogen content measured by effusion. Films deposited at room temperature contain large amounts of hydrogen, yet the defect density of these films is nearly as high as that of evaporated or sputtered a-Si films. This becomes apparent from figure 5 in which the spin density is plotted against deposition temperature T_s (Fritzsche *et al* 1978). The best electronic grade films with lowest $N(E)$ and largest photoconductivity correspond to the minimum in the spin density near $T_s = 300^\circ\text{C}$. A further increase in T_s causes out-diffusion (see figure 2) or a smaller retention of hydrogen and a resulting increase in defect density.

The optimum condition appears therefore to be a compromise between the beneficial effect of higher T_s , which provides higher surface mobility of the reaction species and thus the accommodation of hydrogen at potential defect sites, and the instability of hydrogen bonding. The fact that fluorine does not diffuse out might explain why a-Si:F:H has fewer defect states (Ovshinsky and Madan 1978; Ovshinsky 1979; Madan and Ovshinsky 1980) than a-Si:H and that it can be deposited at somewhat higher T_s .

4. Conductivity

Hopping conduction among localized states, which dominates in evaporated and sputtered a-Si films, should be negligible in a-Si:H because the density of gap states is low. One thus expects the conductivity to be governed by conduction near the mobility edges E_c and E_v . For electrons this leads to

$$\sigma = \sigma_{\min} \exp [-(E_c - E_F)/kT], \quad (1)$$

Figure 5. Spin density in a-Si:H films prepared at different substrate temperatures. The dashed lines show the increase in N_s after annealing the films for 30 minutes at the temperatures indicated. (After Fritzsche *et al* 1978)

where $\sigma_{\min} \sim 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ is the minimum metallic conductivity (Mott and Davis 1979). The relative position of the Fermi energy E_F with respect to the mobility edge E_c or E_v is temperature-dependent because of the nonsymmetric distribution of states above and below E_F and on account of the T -dependence of the mobility gap which is $E_c - E_v = (E_c - E_v)_0 - \gamma T$ above 200 K. For undoped samples E_F is near the centre of the gap where the statistical shift of E_F should be very small and $\delta = \gamma/2$. To first order in T one may write $E_c - E_F = (E_c - E_F)_0 - \delta T$ which yields

$$\sigma = \sigma_0 \exp(-\Delta E/kT), \quad (2)$$

with $\Delta E = (E_c - E_F)_0$ and $\gamma_0 = \sigma_{\min} \exp(\delta/k)$. If we assume that the T -dependence of the optical absorption edge is the same as that of the mobility gap we obtain $\gamma = 4.4 \times 10^{-4} \text{ eV/K}$ (Chmel and Fritzsche, in press) and hence $\sigma_0 \sim 1.5 \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$.

Figure 6 shows the experimental results (Carlson and Wronski 1979) of σ_0 as a function of ΔE for n -type samples containing different amounts of doping. Our n -type as well as p -type samples behave similarly. It is very surprising that σ_0 reaches values near $2 \times 10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$ when E_F is near the gap centre and that it drops exponentially as

$$\sigma_0 = \sigma_{00} \exp(\Delta E/kT_0), \quad (3)$$

with $T_0 \sim 800 \text{ K}$ when E_F moves to the conduction band. There is as yet no satisfactory explanation for this unusual behaviour. In most other amorphous semiconductors σ_0 is of order $10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ (Fritzsche 1974). The Hall mobility (LeComber *et al* 1977; Beyer *et al* 1977) is about $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for undoped samples in agreement with Friedman's theory (1971) and there is no good reason for $\sigma_{\min}$ to be anomalously large. Spear *et al* (1980) made the suggestion that the mobility edge E_c (or E_v) moves toward the gap centre with increasing T because the wave-function overlap is increased by the thermal motion of neighbouring sites. The amount of this temperature shift is proportional to the spread of the band tail states below the mobility edge. A maximum shift of order $\delta_c = 4.6 \times 10^{-4} \text{ eV/K}$ would account for an additional factor $\exp(\delta_c/k) = 1.5 \times 10^2$ which then yields $\sigma_0 = 2 \times 10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$. This effect has not been observed in chalcogenide glasses perhaps because the preparation methods used for them do not change the spread of the band tail states.

The systematic decrease of σ_0 with ΔE shown in figure 6 implies a systematic trend of the width of band tail states. However, an additional effect has to be considered as E_F is shifted closer to E_c (or E_v) by doping. E_F then lies on an increasing slope of the density of states curve and thus moves away from the mobility edge as T is increased. This statistical shift of E decreases the value of σ_0 . Also, at higher doping levels hopping conduction in localized states below the mobility edge lead naturally to a low σ_0 value (Mott and Davis 1979).

Figure 7 shows the spread of magnitudes of σ_0 and the conductivity activation energy which is obtained for undoped samples (Spear *et al* 1980) using different preparation conditions and different reaction chambers. It shows the same trend as figure 6. The large variation of conduction properties of undoped a-Si:H films

Figure 6. Pre-exponential factor σ_0 as a function of the activation energy for various n -type doped a-Si:H films. (After Chmel *et al* to be published)

Figure 7. Pre-exponential factor σ_0 as a function of the activation energy for undoped a-Si:H films prepared in an inductively coupled (O) and a capacitively coupled (x) reaction chamber. (After Spear *et al* 1980)

illustrates our present lack of control of some essential plasma parameters even if the substrate temperature T_s is held constant.

We have assumed so far that the bulk conductivity can be simply obtained from the conductance of the film between two electrodes in a coplanar electrode geometry. This is not the case. In the following we shall discuss how the measured conductance or conductivity depends on prior illumination (Staebler and Wronski 1977), thermal treatments (Tanielian *et al* 1978; Solomon *et al* 1978), surface layers, and the film thickness (Tanielian *et al* 1980 and Ast and Brodsky 1980).

5. Light-induced changes in conductivity

Figure 8 shows the T -dependence of the dark conductivity (Fritzsche 1980) of a $1.2\text{ }\mu\text{m}$ thick layer of n -type a-Si: H deposited on Corning 7059 at $T_s = 300^\circ\text{C}$ in a plasma containing $\text{PH}_3/\text{SiH}_4 = 10^{-5}$. The measurements were carried out in an oil-free vacuum ($10^{-3} - 10^{-6}$ Torr). Coplanar nichrome or carbon electrodes were used below the film or Al electrodes on top. The resistances scale with the electrode spacing which indicates that contact effects are negligible. Below 100°C , $\sigma(T)$ follows equation (2). Heating to 180°C establishes a high conductance state with $\sigma_0 = 0.65\text{ ohm}^{-1}\text{ cm}^{-1}$ and $\Delta E = 0.2\text{ eV}$. After exposing the sample at room temperature for one hour to $\sim 10\text{ mW/cm}^2$ white light, one reaches the low conductance state with $\sigma_0 = 1.3 \times 10^4\text{ ohm}^{-1}\text{ cm}^{-1}$ and $\Delta E = 0.65\text{ eV}$. The cycle can be repeated at will by heating and subsequent illumination at room temperature.

Figure 8. Temperature dependence of the dark conductivity of a $1.2\text{ }\mu\text{m}$ thick film of n -type a-Si: H. The sequence of heating and cooling is indicated by arrows. The low conductance state is reached after illuminating the sample at 25°C with 10 mW/cm^2 white light for one hour. (After Fritzsche 1980; Tanielian to be published)

This effect was first discovered by Staebler and Wronski (1977) and interpreted in terms of light-induced changes of $N(E)$ in the bulk (Staebler and Wronski 1980). They observed similar light-induced changes in the bulk resistance of a-Si:H Schottky barrier photodiodes. Moreover, the photoconductivity was observed to follow a bimolecular recombination kinetics in the high conductivity state and monomolecular recombination in the low state.

These observations argue strongly for the presence of a light-induced change of the density of gap states. This change must involve a substantial concentration of states, at least 10^{17} cm^{-3} , according to the density of states curve of Spear and LeComber (1976) obtained from field effect measurements, in order to effect a change of E_F of the observed magnitude. No accompanying change in the spin density or the optical absorption edge has been found so far.

One notices in figure 8 that light changes both σ_0 and the conductivity activation energy ΔE . The corresponding values lie close to the curve shown in figure 6 although larger changes in σ_0 are sometimes observed.

The magnitude of the Staebler-Wronski effect depends on doping (Tanielian to be published) as shown in figure 9. The ratio of the room temperature dark conductivity after illumination to the conductivity of the annealed state at room temperature is plotted here against the activation energy ΔE of the annealed film. The effect is largest for intermediate doping; it disappears in heavily doped samples and has the opposite sign when the Fermi level lies within 0.2 eV above the centre of the mobility gap. The curve drawn through the experimental points is quite tentative because there are presently only a few points. One notices that the Staebler-Wronski effect of figure 8 is unusually large considering the small ΔE of the annealed state of this sample. It is shown here in order to demonstrate how little we know about the systematic trend of this effect.

Figure 9. Approximate magnitude of the Staebler-Wronski effect as a function of ΔE of the annealed sample (state A). State B is reached after illumination. (After Tanielian to be published)

Before we discuss these results further the effect of space charge layers adjacent to the surface or the substrate interface must be considered.

6. Conducting space charge layers

In the absence of surface states it is conceivable that the bands remain flat up to the surface. In that case adsorbates, oxide, or other overlayers must have a strong effect on the surface potential and produce an electron or hole accumulation layer. When the surface state density is large it would be fortuitous if the surface potential were to coincide with the potential in the bulk material for all doping levels. In general a space charge layer exists and the effect of adsorbates and overlayers on this space charge layer is expected to be reduced in proportion to the number of surface states. The width of the space charge layers is appreciable ($\geq 0.3 \mu\text{m}$) in a-Si: H because of its low density of gap states [$N(E) \leq 10^{17} \text{ eV}^{-1} \text{ cm}^{-1}$].

In the following we describe the effect of overlayers (Tanielian *et al* 1980; Yamaguchi and Fritzsche to be published) and adsorbates (Tanielian *et al* 1978, 1980) on the conductance of a-Si: H films. Since the films were exposed to air between removal from the deposition chamber and mounting in the measuring apparatus, their surface is probably covered with a few monolayers of natural oxide. Before starting the experiment, the effects of light and moisture were removed and a reproducible surface condition was obtained by heating the sample in vacuum to 160°C for about one hour.

Figure 10 shows the decrease in conductance of a $0.36 \mu\text{m}$ thick slightly *p*-type a-Si: H film upon exposure to various gases, H_2O , NH_3 , and dimethyl ether

Figure 10. Relative change of conductance G of a $0.36 \mu\text{m}$ thick a-Si: H film due to exposure to adsorbates. These changes are reversed by annealing in vacuum at 160°C for one hour. (After Tanielian *et al* 1978)

(Tanielian *et al* 1978). Here p/p_0 is the ratio of the partial pressure of the gas to its equilibrium vapour pressure at room temperature. The original conductance state, characterized by $\sigma_0 = 1.5 \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ and $\Delta E = 0.76 \text{ eV}$, can be restored by heat-drying the sample in vacuum at 160°C . The large conductance decrease can be interpreted in two ways. Most of the conductance of the heat-dried sample might have been due to a conducting hole accumulation layer adjacent to the surface which is reduced by the electrons donated by the adsorbed NH_3 or H_2O . Alternatively, the electrons donated by the adsorbates may have produced a space charge layer which extends essentially through the thickness of the a-Si:H film, thereby shifting the Fermi level of the p -type material toward the gap centre (Schiff *et al* to be published). We favour the second explanation because this sample is relatively thin, and the effect is diminished with increasing sample thickness.

H_2O and NH_3 adsorbates act as donors whereas O_2 and Se overlayers are acceptors and remove electrons from the amorphous film. Solid overlayers like Se enable one to measure the conductance over a sufficiently large temperature range so that ΔE and σ_0 can be determined. Moreover, Se can be evaporated from a moderately low temperature source so that the sample is not exposed to light which would cause an undesired photo-induced conductance change.

Figure 11 shows the effect of H_2O (curve 1) and of Se (curves 2 and 3) on the conductance of a $1.14 \mu\text{m}$ thick undoped sample which was slightly n -type (Yamaguchi and Fritzsche, to be published). After heat-drying for 1 hour at 160°C in a vacuum of 10^{-6} Torr we measured $\Delta E = 0.71 \text{ eV}$ and $\sigma_0 = 3.1 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$. The H_2O admitted was 50 Torr of 100% moist He which corresponds to $p/p_0 = 0.067$. This produced an increase in conductance by a factor of six. After 90 minute exposure the moist gas was evacuated which approximately restored the original conductance. After a second heat-drying, Se was deposited onto the sample. This resulted in a decrease in conductance by nearly two orders of magnitude (curve 2). The Se thickness was monitored by a quartz crystal oscillator. At various Se thicknesses the deposition was interrupted in order to measure ΔE and σ_0 . These values are shown in figure 12. It is remarkable that the slope of this line is very close to that of figure 6. In addition, we were surprised to find that more than $1000 \text{ \AA}$ of Se is needed before the interface potential reaches a saturation value. We believe this is because the potential of a heterojunction is established only when both semiconductors are at least as thick as their respective space charge layers. Thus this measurement also provides an estimate of the screening length in Se (Tanielian *et al* 1980).

The deposited Se layer can easily be removed by heating the a-Si:H in vacuum to 160°C . This essentially restores the original conductance of the heat-dried sample. After leaving the sample in a moist atmosphere for 24 hours the conductance of the heat-dried state was found to be lowered by a factor of 10. Se was again deposited in steps which yielded curve 3 of figure 11. The minimum of the curve corresponds to point at which the surface potential is at the intrinsic position near the gap centre. Admittance of H_2O before the minimum was reached increases G , after the minimum it decreases G . This shows that the surface space charge layer turned from n -type to p -type at the minimum. This suggests that the 100 times higher conductance of the original heat-dried state is

Figure 11. Conductance change of a $1.14 \mu\text{m}$ thick heat-dried sample as a function of exposure to He containing 6.7% relative humidity (curve 1 and upper scale). The moist He was evacuated after 90 min marked V. Conductance change as a function of thickness of a Se overlayer (curves 2 and 3, lower scale). (After Tanielian *et al* 1980; Yamaguchi *et al* to be published)

Figure 12. Pre-exponential factor σ_0 as a function of the activation energy of a sample whose conductance was changed by different thicknesses of a Se overlayer (After Yamaguchi *et al* to be published)

due to an electron accumulation layer. If one would assume on the other hand that the bands are flat up to the surface in the heat-dried state, then a conductance decrease by a factor of 100 is only possible if the Se can produce a depletion region which essentially extends throughout the $1.14\text{ }\mu\text{m}$ thick a-Si:H layer. Such a long screening length would correspond to a density of gap states $N(E) \sim 10^{14}\text{ eV}^{-1}\text{ cm}^{-3}$. Although unlikely and at variance with $N(E)$ measured by the field effect, such low values cannot be excluded with certainty at present because the field effect is affected by states in a less than $100\text{ }\text{\AA}$ thick layer of the semiconductor near the substrate interface (Goodman *et al* 1980 and can at best yield an upper limit of $N(E)$.

These samples show that conducting surface space charge regions often dominate the conductance of a-Si:H films. The space charge is greatly affected by adsorbates or insulating layers which either act as donors or acceptors. In films whose thickness is of the order of the width of the space charge region or less, the Fermi level of the whole film is changed with the surface potential. These seemingly disturbing effects are to be expected in high quality films which have low densities of localized gap states. The conductance and other measurements are influenced not only by the space charge region and the potential of the outer surface but also by those near the substrate interface and charges trapped in the insulating substrates as shown by the work of Solomon *et al* (1978). These effects undoubtedly contribute to the scatter of experimental data on transport properties, photoconductivity, and photoluminescence, particularly when films of greatly varying thickness and different thermal history are compared.

7. Field effect

A measurement of the energy distribution $N(E)$ of the density of gap states as a function of doping and preparation conditions is essential for unravelling the origin of the remaining localized states and for determining the width of the space charge layers. Attempts are being made to obtain $N(E)$ by electron tunnelling (Balberg 1980; Balberg and Carlson 1979), by transient deep level spectroscopy (Cohen 1980) and from capacitance-voltage characteristics (Tiedje *et al* 1980; Snell *et al* 1980; Beichler *et al* 1980; Hirose *et al* 1979; Viktorsvitch *et al* 1980).

The field effect (Spear and Lecomber 1972; Spear *et al* 1978; Madan *et al* 1976) was the first method which demonstrated the dramatic decrease in $N(E)$ achieved by the glow discharge deposition technique. It yielded the $N(E)$ curve for a-Si:H which is most often used for interpreting other experimental results. In this section I wish to discuss certain advantages and some limitations of this method.

The idea is straightforward. One uses the insulated-gate field-effect geometry. The insulator has to have a high dielectric strength ($\geq 10^6\text{ V/cm}$) and a leakage current which is small compared to the source to drain current in the amorphous semiconducting film. We use $165\text{ }\mu\text{m}$ thick fused silica plates and minimize ion motion and charge trapping in the insulator by reversing the polarity of the gate potential V_F and checking the conductance at $V_F = 0$ after each measurement as V_F is increased in steps (Goodman *et al* 1980). The a-Si:H surface treatment

has to be chosen to yield a low total conductance so that the field effect at the interface is not short-circuited by a conducting space charge layer at the free surface.

Figure 13 shows (Goodman *et al* 1980) the field effect of a $0.5\ \mu\text{m}$ thick undoped a-Si:H film deposited at 260°C . The measurements were taken at 60°C in vacuum with a source to drain voltage of 50 V and electrode separation of 0.1 cm. For positive field voltages V_F the conduction band edge E_c is bent toward E_F at the quartz interface (electron accumulation). The sample was subjected to the Staebler-Wronski (1977) cycle of illumination and annealing as explained in the figure caption. The magnitude of the Staebler-Wronski effect, which is the conductance change at $V_F = 0$ between curves C and D in figure 13, is quite small in this near intrinsic sample.

Noting the shift of the minimum of the field effect curves one observes that the interface starts out to be slightly *p*-type (curve A). It approaches the flat band condition after four days in vacuum (curve B) and is slightly *n*-type after annealing at 160°C (curve C). Changes in the absolute magnitude of the minimum may be attributed to changes in band bending at the top surfaces. This is disturbing because the interpretation of the results assumes that the conductivity at the free surface is identical to that of the bulk.

After illumination and measuring curve D, the sample was again annealed and subsequent measurements retraced curve C so well that any difference would not show up on this plot. One effect of illumination is the shift of the surface

Figure 13. Conductance as a function of field voltage of a $0.5\ \mu\text{m}$ thick undoped a-Si:H film at 60°C in vacuum. The field voltage is applied across a $165\ \mu\text{m}$ thick fused silica substrate. The curves through the data points are computer fits which yield $N(E)$ of figure 14. (After Goodman *et al* 1980)

potential which yields minimum conductance. This light-induced change of the $V_F = 0$ band bending may be due to a change of the surface potential or of the bulk Fermi level. The fact that the magnitude of the minimum hardly changes with illumination seems to exclude the latter possibility. However, this conclusion requires the proof that the value of the minimum is not determined and fixed by a conducting space charge layer at the free surface. As argued above, the lower minimum of curve A indicates that this sample may have such a surface space charge layer.

Curves C and D do not coincide after shifting their minima to the same value on the V_F axis. The field effect conductance rises less rapidly after illumination (curve D). This corresponds to a light-induced increase of $N(E)$, particularly in the lower part of the gap.

Using an iterative and self-consistent computer program we obtained (Goodman *et al* 1980) a fit to the experimental points which yielded the $N(E)$ curves shown in figure 14. $N(E)$ of curve D is indeed somewhat larger than that of curve C at some energies. Since our $G(V_F)$ curves are steeper at negative V_F (hole conduction) than at positive V_F (electron conduction) we obtain a lower $N(E)$ below the gap centre than above in contrast to the results of Spear *et al* (1978) and Madan *et al* (1976).

Figure 14. Density of states curves $N(E)$ corresponding to computer fits shown with the data in figure 13. (After Goodman *et al* 1980)

The detailed structure revealed by the $N(E)$ curves of figure 14 could convince anyone of the value of field effect measurements for determining important features of the localized state distribution. Unfortunately, this is not the case as I shall explain in the following.

We felt that the number of data points taken could not possibly be sufficient to reveal the detailed structure shown in figure 14. We generated by hand a smooth $N(E)$ from curve D of figure 14 and calculated $G(V_F)$. These are shown in figure 15 together with the experimental data of the illuminated sample (D of figure 13). The fit is not perfect and less good than that shown in figure 13 but the deviations are within the experimental error of the data. A true computer fit to real data takes each point too seriously, trying to fit each one as well as possible. This can generate spurious structure in $N(E)$. On the other hand, we cannot exclude the possibility that the true $N(E)$ curve has even more pronounced structure than that shown in figure 14. In some computer experiments we have obtained such $N(E)$ curves which also produced very good fits to the data points. We believe that field effect measurements cannot truly determine detailed structure in $N(E)$ because of the smoothing effect of integrating Poisson's equation and the kT broadening of the Fermi function.

Nevertheless, field effect measurements were able to demonstrate that $N(E)$ decreases with increasing deposition temperature T_s in the glow discharge system (Madan *et al* 1976 Spear and LeComber 1972, 1978) as well as the beneficial effect of fluorine in a-Si:F:H. Moreover the general reproducibility within a factor 3-5 of $N(E)$ obtained by us and by Spear *et al* (1978), after averaging out some structure observed here and there, suggests that the magnitude of $N(E)$ is

Figure 15. Fit of $G(V_F)$ data D of figure 13 with the structureless $N(E)$ shown here. (After Goodman *et al* 1980)

indeed roughly correct. If the field effect does not measure $N(E)$ of the bulk material then some assumptions underlying our analysis must be incorrect. Let us explore this in the following.

In figure 16 we show (Goodman *et al* 1980) the field effect current integrated to a distance x from the interface for various surface potentials, V_0 , produced by the field voltage V_F . These curves were all calculated for the $N(E)$ published by Spear *et al* (1978). Surprisingly, for many values of V_0 more than 90% of the field effect current flows within the first 50 Å layer adjacent to the interface even though the space charge layer is about one and a half orders of magnitude wider. This is because the band bending potential appears in the exponent of the conductance integral and is largest at the interface.

The narrowness of the current channel makes relevant the question whether $N(E)$ of the initial layer deposited onto the substrate is the same as that of the bulk material. The plasma chemistry governing the film growth may be different on the substrate and on the growing a-Si:H surface. This question can be settled by comparing the field effect near the substrate interface with that near the top surface. Preliminary results obtained at TIFR in Bombay (Guha, private communication) indicate that the top and interface field effects are essentially the same if the top surface is annealed for several hours in vacuum at 180° C to remove adsorbates.

The analysis of the field effect assumes that all gap states and extended states are shifted by the potential $V(x)$ without a change in localization or mobility. Essentially one assumes that the mobility edge follows $V(x)$ up to the surface. In the current channel responsible for the field effect one deals essentially with a narrow quasi-two-dimensional potential well. The quantum states in the well

Figure 16. Integrated field effect current as a function of the distance from the interface, x , for various interface potentials V_0 . (After Goodman *et al* 1980)

will be strongly affected by the boundary conditions as in the case of silicon inversion layers (Stern 1972). We presume therefore that states will remain localized in the potential trough up to higher energies and that the mobility edge meets the interface with zero slope instead of following $V(x)$. This places the mobility edge further away from E_F than $E_F - |eV(x)|$. If that is so, we overestimated $N(E)$ in the range of large band bending. We hope that measurements of $N(E)$ by other methods will soon become available to answer these questions.

8. Concluding remarks

As the quality of gas-phase deposited a-Si:H is being improved, the material has to be prepared and characterized with the same care commonly given to crystalline semiconductors. Since the material can be prepared only in the form of thin films, great attention has to be paid to the space charge layers at the surface and substrate interface. They strongly affect a large number of measurements and may have been the reason for the large scatter and irreproducibility of what were assumed to be bulk properties. Insulating overlayers, which act as donors or acceptors, may be used to eliminate existing space charge regions and to passivate the amorphous semiconductor against the effects of ambients.

The light-induced changes of the conductivity and photoconductivity of a-Si:H films appear to be associated with changes in the localized gap states. This interesting phenomenon is presently complicated by simultaneous light-induced changes of the surface potential and conducting space charge layers. These effects appear to be associated with the presence of hydrogen and of substitutional dopants.

The determination of the energy distribution of localized gap states and the elucidation of their origin remain important tasks. If interpreted with caution, the field effect is a valuable tool for determining the value of and changes in the interface potential. It provides an upper limit of the localized state density $N(E)$ in a 50–100 Å thin layer adjacent to the interface or surface. $N(E)$ determined by the field effect alone is not able to reveal the possible presence of detailed structure in the density of states function.

There is little doubt that the substitutional doping of a-Si:H and a-Si:F:H has opened an exciting new field for technical applications and fundamental studies of amorphous semiconductors.

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