Study of the density of states in amorphous Silicon-Hydrogen using the semiconductor/electrolyte system

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Abstract

Localized states in amorphous Silicon-Hydrogen are studied by pulsed measurements on the a-Si:H/electrolyte (S/E) system. The S/E interface is essentially blocking to current flow. As a result, surface space-charge layers, ranging from large depletion to very strong accumulation conditions, can be induced and studied. Measurements in the depletion range under illumination yield directly the total density of occupied states in the entire energy gap. This is useful in obtaining a quick and reliable assessment of the quality of the amorphous films. In high grade films we find that the total density of occupied states is around 10^{18} cm^{-3}. The data in the accumulation range, on the other hand, provide useful information on unoccupied states near the conduction band edge.

Estudio de la densidad de estados en silicón-hidrógeno amorfo usando el sistema semiconductor/electrólito

Sinopsis

En este artículo estudiamos estados localizados en silicio amorfo hidrogenado (a-Si:H) utilizando el sistema semiconductor/electrólito (S/E). La interfase del semiconductor electrólito se opone al flujo de corriente y como resultado se puede obtener capas de cargas espaciales superficiales, que van desde la extracción hasta condiciones de acumulación fuerte y permiten estudiarlos e inducirlos. Medidas en el alcance de extracción bajo iluminación ceden directamente los estados ocupados en la zona prohibida de energía del semiconductor. De esta manera podemos tener una mejor idea de la calidad del material semiconductivo. En películas de alta calidad hemos podido obtener

una diversidad de estados ocupados de alrededor de 10^8 cm $^{-3}$. Los datos en el área de acumulación nos proveen información útil de los estados no ocupados cerca de la banda de conducción.

Introduction

Considerable effort has been devoted to derive the density of states spectra in an amorphous Silicon- Hydrogen (a-Si:H) films (Madam, and Shaw, 1992). For this purpose use is made of pulse measurements on the semiconductor/electrolyte (S/E) system. Such measurements, which proved to be very useful in the study of crystalline semiconductors (Wolovesky, et al., 1986), have been found to be equally effective when applied to a-Si:H films. The blocking nature of the S/E interface allows the induction of applied bias space-charge layers at the a-Si:H surface, ranging from large depletion to very strong accumulation conditions. In this manner, the entire energy gap in the space charge region, together with its localized states, can be swung below and above the Fermi level. At the same time, it is possible to measure the surface space-charge density Q_{sc} as a function of the barrier height V_s. In a-Si:H, Q_{sc} resides predominantly in the localized states (except in strong accumulation conditions); thus the measurements yield, at least in principle, the energy distribution of the density of states.

High grade device quality films are usually close to intrinsic. Such high resistivity films cannot be handled by our measurement technique because the surface space-charge capacitance cannot be charged within the short duration applied pulse biases. Accordingly, most of the results to be reported here have been obtained under illumination, for which the photo resistivity is typically 105 ohm-cm or less. Our results in the depletion range remarkedly agree with the theoretical curve that takes into account the presence of localized states. The data thus yield directly the total density of occupied states in the entire energy gap. This is very useful in obtaining a quick and reliable assessment of the quality of the amorphous films. In high grade materials we find that the total density of occupied states is around 10^{18} cm^3. The results in the accumulation range, on the other hand, provide useful information on the unoccupied states near the conduction band edge. Analysis of the data in this case, however, is more difficult because surface states are apparently also involved.

Amorphous Silicon - Hydrogen (a-Si:H)

Attention is focusesd on the energy region between the top of the valence band and the bottom of the conduction band, the region of greatest interest to semiconductor physics. Figure 1 sketches the density of electron energy states N(E). Ev and Ec are the mobility edges of the valence band of the conduction band and the conduction band, respectively. This is essentially the distribution of energy of the CFO model that was proposed by Cohen, Fritzsche, and Ovshinsky in 1969. Since that time, much has been learned about the many details of specific defect states (Schwartz, 1988). Both the conduction band and the valence band have tails of states, and deeper in the gap there are states originating from structural and coordination defects (atoms which are not bonded according to their normal valence) as well as from impurities. Hence, in contrast to crystals, N(E) is nowhere zero.

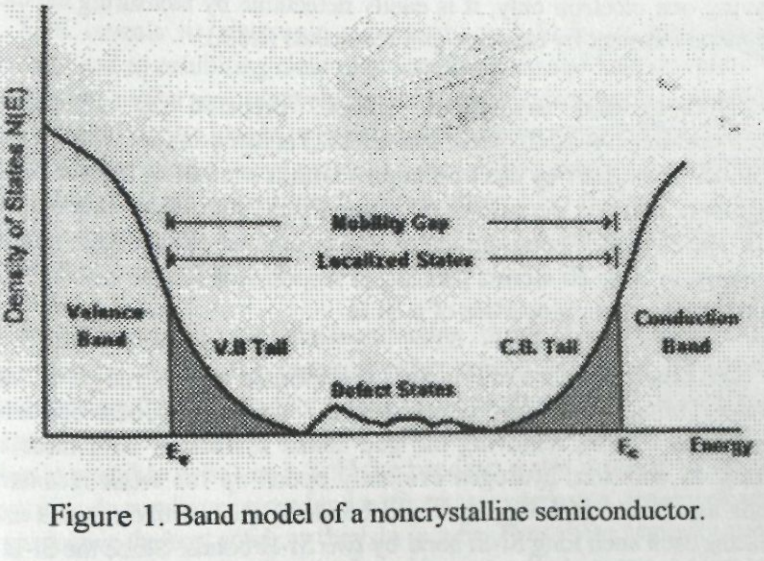

Figure 1. Band model of a noncrystalline semiconductor.

It is believed that the tail states are unavoidable because they are intimately associated with disorder in the non-crystalline structure. The valence band tail states are covalent bonds that are weaker than normal. This can happen, for instance, when the covalent angle is bent from its equilibrium value, when the bond is stretched due to internal strains, or when some anti-bonding orbital is mixed in. That occurs, for instance, when the atoms bond together in odd-numbered rings containing 5, 7, and 9 atoms (instead of the 6 atoms in crystals). Moreover, it was recently found, both theoretically and experimentally, that there are net static charges on some atoms or groups of atoms (Schwartz, 1988). These produce potential fluctuations which push states up and down and prevent any sharp feature in N(E). All these effects are expected to produce tail of states extending down in energy from the conduction band.

A typical defect-related gap state is a dangling bond, that is, a Si atom bonded to only three nearest neighbors instead of four. Since the dangling bond state is not bonded (and not anti-bonded), it lies near the gap center. Having one electron only, it is easily detectable by measuring the electron magnetic moment by electron spin resonance (ESR).

Hydrogenated amorphous silicon, prepared by glow-discharge decomposition, has molecules of silane (SiH_4) at low pressure within a vacuum chamber, torn apart by electron impact within alternating electric field. The fragments react on the surface of a heated substrate, depositing a film of a-Si:H. The chemical incorporation of a large amount of hydrogen, typically in the range of 3 to 20 atomic percent, is responsible for the beneficial effect upon the electronic properties of a-Si:H.

The beneficial action of H in Si-H is attributed to the strength of the Si-H covalent bond. Hydrogen terminates the dangling bonds occurring in amorphous silicon, removing the gap states associated with these native defects. In addition, hydrogen evidently opens up the weak reconstructed bonds associated with the voids and bonds to those silicon atoms as well, replacing each such long Si-Si bond by two Si-H bonds. Since the Si-H bond is very strong and its bonding anti-bonding splitting is larger than that of Si-

Si, the states introduced by the Si-H bonds lie at energies which are outside of the bandgap region of the a-Si "host " (Schwartz, 1988). The effect of all of this is to wipe out most of the electron states in the gap which the network defects native to a-Si would normally introduce.

In addition to mopping up the bandgap states derived from the structural deviations from the ideal four-coordinated continuous random network, there is an additional aspect to the beneficial action of bonded hydrogen in a-Si:H. Hydrogen, in a-Si:H, enters into the network structure and changes it, causing a reduction in coordination, the covalent network is less over constrained than is the network in pure amorphous silicon. As a result, the bond angle strain in a-Si:H is less than it is in a-Si. Since tailing of N(E) into the gap region in a-Si attributed, at least in part, to the distribution of Si-Si-Si bond angles in the random network structure, the narrowing of this distribution in a-Si:H reduces the extent of the tailing and thus provides another mechanism by which the incorporation of hydrogen cleanses the solid of states in the gap.

Si-H reveals its electronic superiority to a-Si in its high electrical resistivity and in exhibiting clear photoconductivity and luminescence. With its energy gap region now relatively free of states, the temperature dependence of its conductivity no longer resembles the variable range hopping behavior seen for a-Si but instead obeys a standard exp(-E/kT) semiconductor behavior with E about half the optical gap E_0. (E_0 is about 1.5-1.9 eV for typical Si-H glasses, compared to 1.3 eV for a-Si). Transport is dominated by extended states rather than by localized states as in a-Si.

Most important, the semiconducting properties of a-Si:H can be controlled by doping the material either n-type or p-type by chemically incorporating either column-five donors (such as phosphorus) or column-three acceptors (such as boron) in much the same way as in crystalline silicon. What makes it possible is that in a-Si:H the bandgap states inserted by the dopant impurities do not have to contend with an overwhelming density of states in the gap native the host solid, as they do in a-Si. Thus these impurity states are able to push the Fermi level around, and in particular to move it close to E_c or E_v, allowing a-Si:H to act as an n-type or p-type extrinsic semiconductor.

Solid/liquid interface

The semiconductor/electrolyte interface systems offer several distinct advantages for certain studies of the semiconductor interface. The primary advantage is that the surface preparation and the measurements are carried out in one and the same medium, so that the sources of irreproducibility inherent in the usual postech procedures of rinsing, drying, handling, etc., are eliminated. Another important advantage is that the use of an electrolyte to make contact with a semiconductor yields one of the most important effective blocking contacts.

A third advantage stems from the fact that the ion concentration in the electrolyte may readily be made so high that the screening length is much less than that of the semiconductor. The only significant potential drop in the liquid phase is then the one across the very thin "Helmholtz layer" of absorbed ions or molecules and the "Guoy layer".

All changes in potential affect the potential drop across the semiconductor/electrolyte interface. At a fixed applied potential there are regions of varying electrical potentials (fig. 2). The Gouy layer is the thickness of electrolyte where the ion concentration donates from the bulk electrolyte values. In aqueous electrolyte with typical supporting electrolyte concentrations of 0.1 molar or greater, this layer is extremely thin (on the order of 10A), and the potential drop across this layer can be neglected. The Helmholtz layer is the region between the electrode surface and the plane of closest approach for ions. Within the electrode there is a space charge layer, in which the electrical potential varies from the surface to the bulk value. The term "space charge" refers to the presence of a charge occupying the volume near the surface; the charge results from the charged doping sites or the accumulation of holes or electrons near the surface. The potential changes smoothly across the width of the space charge layer. Because an electron at a band edge exhibits different energies in regions of varying electrical potentials the band edges bend accordingly. The band bending can be positive or upwards, with E_c and E_v higher at the surface than in the bulk, or the band-bending can be downwards (negative). The magnitude of the band bending

($E_{c,s}$ - $E_{c,b}$, where s and b refer to surface and bulk) is equal to the total potential drop across the space charge layer. An important consequence is that the hole and electron concentrations are perturbed at the surface relative to the bulk. The Fermi level stays at constant energy from the bulk to the surface, so the position of the Fermi level relative to the band edges changes at the surface. For the case of positive band bending shown in figure 2, electrons are depleted and holes enriched.

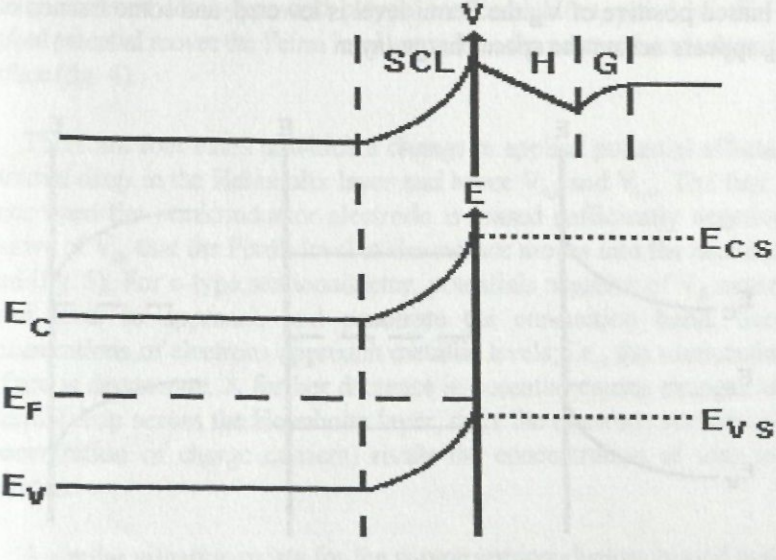

Figure 2. Electrical potential drops across the semiconductor/electrolyte interface and band bending. The upper curve shows the electrical potential across the interface. SCL = space charge layer; H = Helmholtz layer; G = Gouy layer. The relative thickness of these layers is not shown to scale. Ec,s and Ev,s mark the surface energies of the conduction band edges, respectively.

A change in the externally applied potential results in a change in the potential drop across both sides of the interface, but in certain cases the change is confined largely to the space charge layer in the semiconductor. In accordance with double layer theory, the side of the interface containing the lower concentration of charge carriers experiences the greater change in potential when the applied potential is modulated.

For any given semiconductor and electrolyte, there exists a unique potential for which the potential drop between the surface and the bulk of the electrode is zero (no space charge layer). This potential is called the flat band potential (V_{fb}), since the band edges do not bend (fig. 3). When the electrode is biased positive of V_{fb} the Fermi level is lowered, and some fraction of V - V_{fb} appears across the space charge layer.

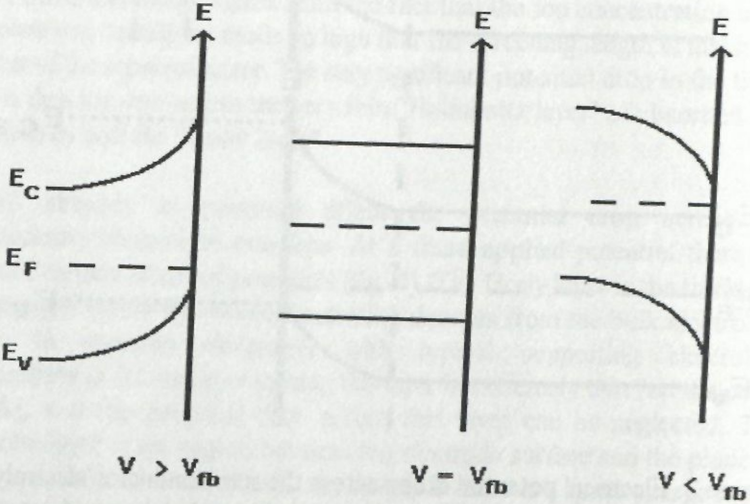

Figure 3. Band bending as a function of applied potential. V=applied potential; V_{fb} = flat band potential. Intrinsic semiconductor.

Because the electrical potential is lower in the bulk than at the surface, the band edges bend upwards. Likewise, applied potentials negative of V_{fb} cause downward band-bending. If the semiconductor is intrinsic, as shown in figure 3, and relatively free of surface states (energy levels on the surface and in the band gap region), then the potentials change relative to V_{fb} appear in the space charge layer. In this situation the magnitude of bandbending in eV equals the change in applied potential with respect to V_{fb}.

$$E_{c,s}-E_{c,b}=q(V-V_{fb}) \tag{1}$$

Thus the direction and magnitude of band-bending can be predicted by knowing the applied potential relative to V_{fb}. The highly desirable condition is also obtained for n-type and p-type semiconductors, provided that the applied potential moves the Fermi level away from the nearest band edge at the surface (fig. 4).

There are four cases in which a change in applied potential affects the potential drop in the Helmholtz layer and hence $V_{c,s}$ and $V_{v,s}$. The first two occur when the semiconductor electrode is biased sufficiently negative or positive of V_{fb} that the Fermi level at the surface moves into the near energy band (fig. 5). For n-type semiconductor, potentials negative of V_{fb} cause the Fermi level to approach and penetrate the conduction band. Surface concentrations of electrons approach metallic levels; i.e., the semiconductor surface is degenerate. A further decrease in potential causes changes in the potential drop across the Helmholtz layer, since the electrode surface charge (concentration of charge carriers) rivals the concentration of ions in the electrode.

A similar situation exists for the p-type semiconductors biased positive of V_{fb}. Likewise, under conditions of extreme band bending (positive for n-type, negative for p-type), the surface Fermi level moves into the further energy band. Again the electrode surface becomes degenerate, but with holes instead (carriers inversion). The fourth case arises when there exists a high density of surface states within the bandgap region. When the Fermi level is located at the same energy as the surface states, then occupancy of the surface states and the surface charge becomes sensitive to the applied potential. In extreme cases, all of the external potential change appears across the Helmholtz layer and the surface states. The band bending is fixed, and the band edge position appears to be no longer independent of potential. This situation is called Fermi level pinning, since the surface position of the Fermi level is pinned with respect to the band edges (fig. 5c).

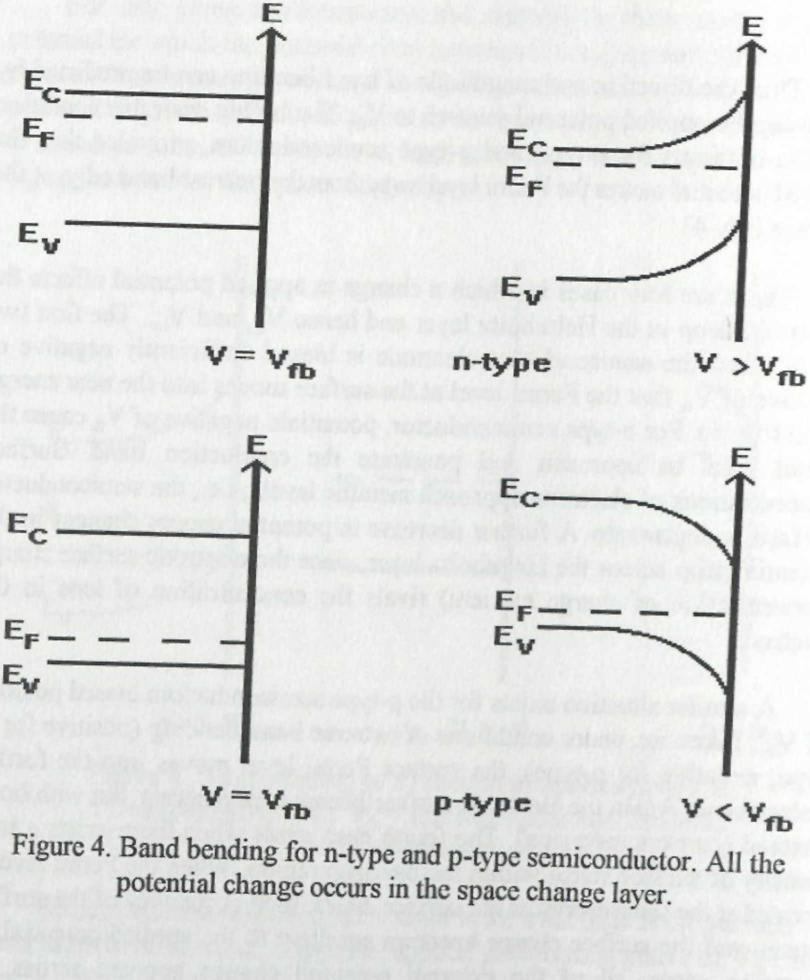

Figure 4. Band bending for n-type and p-type semiconductor. All the potential change occurs in the space change layer.

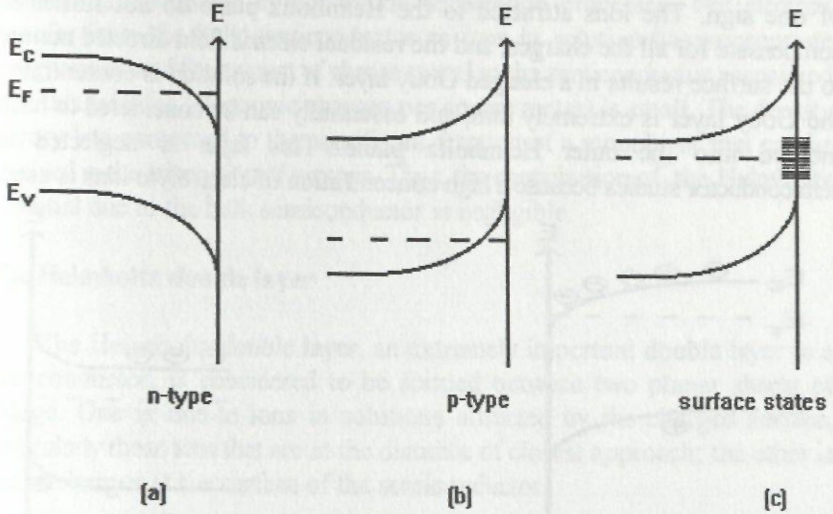

Figure 5. Band bending leading to degeneracy in (a) n-type and (b) p-type semiconductor, and (c) Fermi level pinning by the surface.

Band bending determines whether majority carriers or minority carriers move towards the electrode surface. We consider now the case of an n-type semiconductor without Fermi level pinning. At potentials more negative than Vfb, the majority carriers, electrons in the conduction band, flow towards the electrode surface to form an accumulation layer (fig. 6a). The Fermi level moves into the conduction band at the surface. The high concentration of charge carriers endows the surface with metallic properties. When the applied potential moves positive of V_{fb}, the charge carrier flow reverses, and now minority carriers (holes) accumulate at the surface. Since the majority carriers are removed from the surface, the space charge layer is called an exhaustion or depletion layer (fig. 6b).

The Gouy layer

The Gouy layer describes a region in the solution (fig. 2) near the semiconductor in which there is a space charge due to an excess of free ions of one sign. The ions attracted to the Helmholtz plane do not suffice to compensate for all the charges, and the residual electric field directed normal to the surface results in a charged Gouy layer. If the solution is concentrated the Gouy layer is extremely thin, and essentially can be considered to have melded into the outer Helmholtz plane. This layer is neglected in semiconductor studies because a high concentration of electrolyte ions is used.

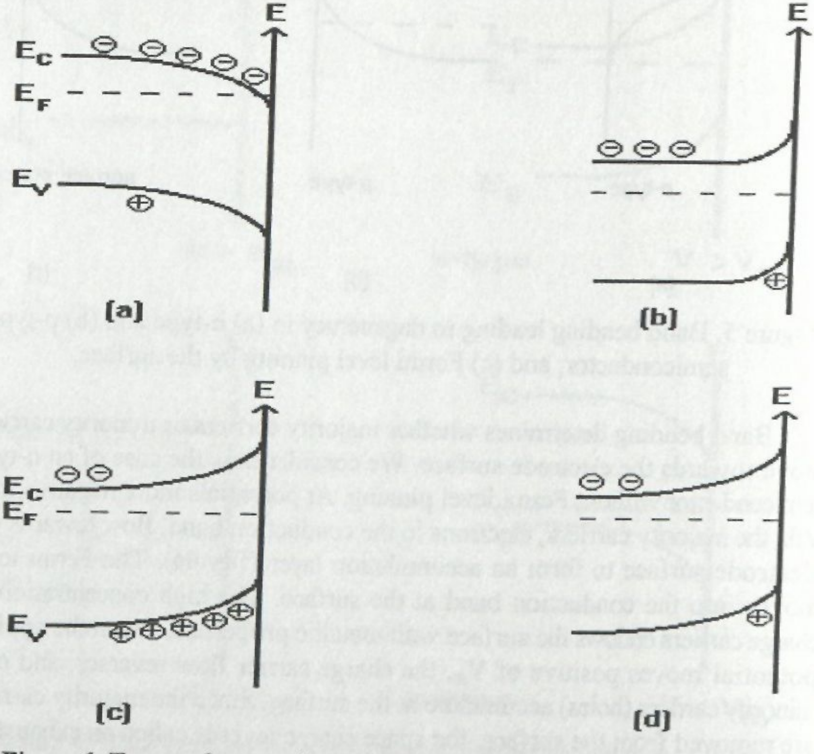

Figure 6. Types of space charge layers in a n-type semiconductor (a) accumulation layer, (b) depletion layer, (c) inversion layer, (d) deep depletion layer.

In a semiconductor, there is a possibility that either the adsorption/description or electron transfer could control the Helmholtz potential. It turns out that for a non-degenerate semiconductor the Helmholtz potential is dominated by adsorption/desperation processes. The electron transfer from the bulk semiconductor to ions in solution has appropriate energy values and the amount of charge stored in the semiconductor associated with this transfer (electronic charges per square meter) is small. The density is very low compared to the significant fraction of a monolayer that can be involved in the adsorption of protons. Thus, the contribution of the Helmholtz potential due to the bulk semiconductor is negligible.

The Helmholtz double layer

The Helmholtz double layer, an extremely important double layer in a semiconductor, is considered to be formed between two planar sheets of charge. One is due to ions in solutions attracted by the charged surface, particularly those ions that are at the distance of closest approach; the other is due to charges at the surface of the semiconductor.

The charge on the planes (fig. 2) is of several forms. On the solution side of the Helmholtz double layer, the charge originates by the accumulation of ions on the ohp (outer Helmholtz layer). On the solid side of the Helmholtz double layer, the charge can arise in three forms: an accumulation layer of free charge, free charge trapped from the solid into the surface states, or adsorbed ions. The form that dominates varies with the semiconductor. With these mechanisms of charging, the concentration described above can be easily reached. Concentrations of excess charge in this magnitude almost appear in the space charge region of a non-degenerate semiconductor.

a-Si:H sample preparation

Device quality a-Si:H films were prepared by glow-discharge decomposition of silane. First, a thin n+ layer was deposited on a conducting glass substrate, followed by a 1-mm thick intrinsic film. The n+ layer provides an ohmic contact between the conducting glass and the intrinsic film. The conducting glass was cut into squares of about 0.5 cm^2; a wire contact was attached to the conducting glass. The wire lead, contact area and the entire sample were masked by an epoxy cement, except for a small area (~2 mm^2) of the film's surface to be exposed to the electrolyte. The sample and a platinum electrode were immersed in an indifferent electrolyte such as $Ca(NO_3)_2$. The sample was illuminated through the transparent electrolyte by a ~2 mW He-Ne laser.

Experimental arrangement

A schematic diagram of the experimental arrangement is displayed in figure 7. The semiconductor sample and platinum electrode are immersed in a $Ca(NO_3)_2$ electrolyte. Because of the masking described above, only a small area of the sample is exposed to the aqueous solution. The platinum electrode is in the form of a sheet of large surface area (2cm^2). The pulse generator (Hewlett-Packard type 214A) can provide positive and negative pulses up to 100V in amplitude and 0.05 to 200 μsec in duration. It is connected to the platinum and semiconductor electrodes via a diode D and a large (0.1 to 1μF) series capacitor C. The diode polarity is such as to permit current flow only while the pulse is on. An electronic switch S can short-circuit the Pt electrode to ground at any prescribed time following the termination of the pulse. Short-duration pulses were applied singly, in order to minimize any electrochemical reactions that may take place at the silicon surface.

A Tektronix type 7407 CRO was used to monitor the voltage drop V_a between the Pt electrode and the ohmic contact of the sample, and the drop V_c across the series capacitor C. Strictly speaking, the relevant oscillogram is that of the voltage drop V_a between a reference electrode and the sample, rather than $V_{a'}$. However, the space-charge capacitance at the platinum surface is orders of magnitude larger than that at the semiconductor surface. Hence, only a negligible fraction of the applied bias is expected to drop across the Pt/electrolyte interface, so that the two traces should yield practically identical results. This was indeed checked to the case by the occasional use of a reference electrode.

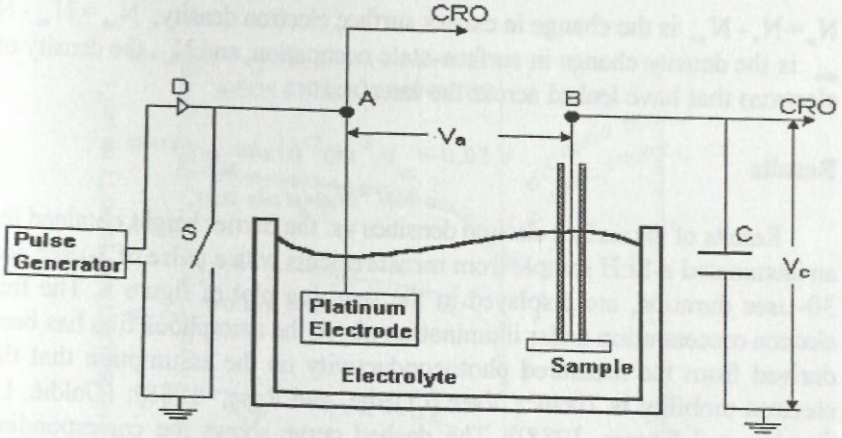

Figure 7. Schematic diagram of the experimental setup

In most cases a space-charge layer exists at the semiconductor surface, characterized by an equilibrium barrier height V_{so} and a space-charge density Q_{sco}. If surface states are present, there may also be an equilibrium surface state charge of density Q_{sso}. The voltage pulse, of amplitude anywhere between 0 and 100 V, charges up the semiconductor surface region. The voltage drop V_a measured just after the termination of the pulse represents to a very good approximation the change $V_s = V_s - V_{so}$ in barrier height induced by the applied pulse. (We assume for the moment that there is no foreign layer such as an oxide layer at the semiconductor surface.) The voltage drop V_c across the series capacitor C, again measured just after the termination of the pulse, yields the overall charge Q_{tot} (= CV_c) passing through the system. The charge density Q_{tot} (per unit area) is obtained by dividing Q_{ot} by the area of the semiconductor surface exposed to the electrolyte.

As suggested above, Q_{tot} is made up in general of the three components: $Q_{tot} = Q_{sc} + Q_{ss} + Q_L$, where $Q_{sc} = Q_{sc} - Q_{sco}$ is the change in space-charge density, $Q_{ss} = Q_{ss} - Q_{sso}$ is the change in the surface-state charge density, and Q_L is the density of the charge leaked across the semiconductor/electrolyte interface. In terms of electron densities, this can be re-written as $N_{tot} = N_s + N_{ss} + N_L$, where N_{tot} is the total electron density passing through the system,

$N_s = N_s - N_{so}$ is the change in excess surface electron density, $N_{ss} = N_{ss} - N_{sso}$ is the density change in surface-state occupation, and N_L the density of electrons that have leaked across the interface.

Results

Results of the surface electron densities vs. the barrier height obtained for an illuminated a-Si:H sample from measurements with a pulse of 3-μsec and 30-μsec duration, are displayed in the semi-log plot of figure 8. The free electron concentration under illumination nb_1 in the amorphous film has been derived from the measured photoconductivity on the assumption that the electron mobility is 10cm^2 / Vsec.[(Tiedje, and Rose, 1988); (Goldie, Le Comber and Spears, 1988)]. The dashed curve shows the corresponding theoretical dependence of the surface electron density N_s on barrier height V_s, as obtained from a solution of Poisson's equation (Wolovesky, et al., 1986) in the absence of localized states. The experimental points are seen to lie well above this curve indicating, as expected for amorphous films, that the space-charge layer in both the depletion and accumulation ranges is dominated by localized states.

When a depletion layer is formed (by an applied negative pulse), free and trapped electrons are expelled from the surface region, leaving behind the positively-charged, localized states that make up the immobile space-charge in the depletion layer. Consider first the case of a non-illuminated sample. The first process that occurs following the application of the negative pulse is the expulsion of the free electrons from the surface region. As a result, there is a net thermal emission of trapped electrons from localized states into the conduction band, and the emitted electrons are, in turn, swept away from the space-charge region. Only shallow states, down to 0.3 to 0.4 eV below the conduction band edge, are able to do so within the measurement time (the pulse duration) (Goldie et al., 1988). Under illumination, on the other hand, the situation is quite different. Hole-electron pairs are continuously generated by the light. The electrons are expelled from the surface region, while the holes are attracted to the surface where they can recombine with the trapped electrons.

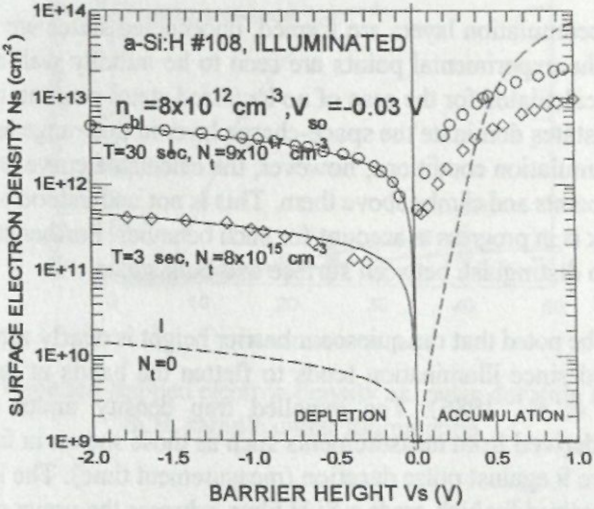

Figure 8. Surface electron density N_s vs. Barrier height V_s in an illuminated sample of a-Si:H

In this manner electrons in occupied states throughout the energy gap can be discharged and expelled from the space-charge layer, irrespective of the depth of the states. The only factors that determine which and how many states can release their trapped electrons within the measurement time are the hole capture cross sections of the states and the hole trapping kinetics. According to figure 1, for a measurement time of 3μsec only a fraction of the trapped electrons are expelled, but when the pulse duration is extended to 30 μsec, practically all occupied states in the depletion layer are discharged and expelled. The solid curves, passing in each case through the points, were calculated from Poisson's equation for the case in which localized states of densities N_t (as marked) are present (Wolovesky, et al., 1986). The agreement between theory and experiment is seen to be remarkably good, adding considerable confidence to our analysis. The total density of occupied states in the entire energy gap, as derived from the data for the 30μsec measurements time, is about 10^{18} cm^{-3}, which is expected value for the films studied.

When accumulation layers are formed, unoccupied states are filled up. Here again, the experimental points are seen to be initially well above the dashed curve calculated for the case of no localized states present, indicating that localized states dominate the space-charge layer in this range as well. At stronger accumulation conditions, however, the calculated curve crosses the experimental points and climbs above them. This is not understood at present, and more work is in progress to account for such behavior. Further studies are also needed to distinguish between surface and bulk states.

It should be noted that the quiescent barrier height is nearly zero. This is to be expected since illumination tends to flatten the bands at the surface (Wolovesky, et al., 1986). The expelled trap density under depletion conditions, as derived from measurements such as those shown in figure 8, is plotted in figure 9 against pulse duration (measurement time). The lower two curves were obtained for high-grade a-Si:H films, whereas the upper curve was obtained after a film has been degraded by the application of many voltage pulses. In all causes, the expelled trap density increases with pulse duration, but tends to saturate at a pulse duration of 30 to 40 μsec. We interpret the saturation level as representing the total density of occupied states in the energy gap. We are in the process of developing a model involving the hole trapping kinetics in order to account for the shape of the experimental curve. Such a model might yield an estimate of the average cross section for hole capture by the occupied states.

The results depicted in figure 10 are similar to those in figure 8, except that they were obtained for a non-illuminated sample. The low dark resistivity necessary for the application of our pulse technique has been achieved in this case by degrading the film. Here we find a rather high density of occupied states, as expected for poor quality material. Since the sample is in the dark, the trapped electrons must now be discharged through thermal emission into the conduction band edge (Wolovesky, et al., 1986).

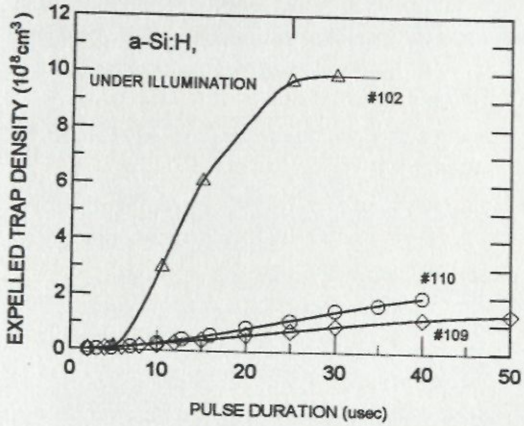

Figure 9. Expelled trapped electron density vs. pulse duration for three a-Si:H sample under illumination.

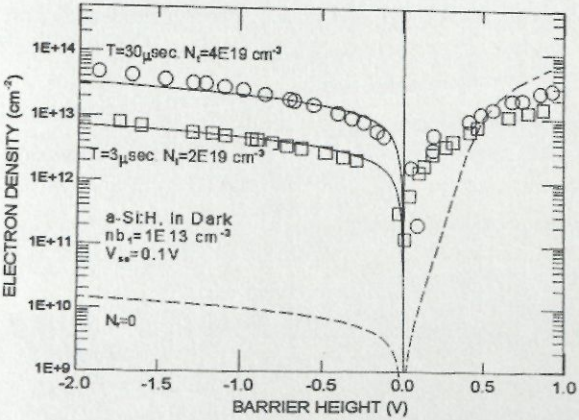

Figure 10. Surface electron density N_s vs. barrier height V_s in a non-illuminated sample of a-Si:H.