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STUDY OF IN-GAP STATES IN HYDROGENATED AMORPHOUS SILICON BY THERMALLY AND OPTICALLY STIMULATED CURRENT MEASUREMENTS

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Gap states in hydrogenated amorphous silicon (a-Si:H) are investigated by thermally stimulated currents (TSC) in the temperature range from 77K to 350K. Our technique uses both optical excitation (infrared and visible light) and electrical biasing to fill traps and create TSC from gap states located in the collecting zone of Schottky barriers built on a-Si:H. Optical emptying is also performed at 77K and the result analyzed on TSC spectra.

1. Introduction

Density of states within the pseudo gap of hydrogenated amorphous silicon has been the subject of intense work during the last years. Such techniques as field effect [1], measurement of capacitance versus voltage and frequency [2], have been utilized for these studies. It is now well established that transport properties in this semiconductor are mainly determined by these gap states rather than by the amorphous structure itself. Roughly speaking shallow traps are the limiting factor for carrier mobility (μ) while deep traps are the limiting factor for the life time (τ) of these same carriers. This leads to a well determined $\mu.\tau$ product to which photoconductivity is proportionnal. It is thus important to characterize the trapping centers as fully as possible (thermal capture cross section, optical capture cross section, energy, eventually associated lattice relaxation, spatial distribution etc...). Presently field effect measurements give a global knowledge of the state density but are unable to distinguish between surface states and volume ones. Features reported by Spear et al. are under contestation for this very reason. Capacitance measurements are sensitive only to middle gap states ($E_{Fi} \pm .1eV$) and also do not distinguish between surface and volume states. In this paper we report on a number of simple experiments which rely on thermally stimulated currents.These experiments allow direct observation of localized state energy levels in a-Si:H by using Schottky structures and were initially suggested by Lang and the present author [3,4]. They might well be considered as a basis for a real localized state spectroscopy analogous to the technique which is currently under development for single crystal semiconductors [5,6].

2. Experiments and comments :

Following structures were used :

Pt/a-Si:H/a-Si:H n^+
8nm 1000 nm 30 nm

They are fully prepared only by cathodic sputtering and have been described elsewhere [4].

Principle of experiments :

Traps are filled up at 77K by different methods (optical or electrical ones) then the diode is heated up at a constant rate β ($.05\ K_S^{-1} < \beta < .5K_S^{-1}$), and a definite parameter continously recorded. This parameter may be short circuit current I_{SC}, capacitance at a given frequency...

Typical continuous plots thus obtained are shown in Fig.2 only for illustration purpose. If retrapping is negligible and if thermal capture cross section is a slowly varying function of temperature (which we have verified (7)) the trap activation energy E_T as in the case of single crystal semiconductors is given by equation (1) which has been derived from (8).

$$\Delta E_T \simeq 23\ k\ T_M, \quad (1)$$

where k is Boltzman constant, T_M is the temperature at the maximum of current TSC.

Fig.2 which shows typical TSC spectrum will be discussed later on. It is worthwhile noticing that for amorphous semiconductors the density of states within the gap is much higher than in crystals. As a consequence the shape and width of space charge may be drastically changed when all traps are filled up, and hence the TSC spectrum may be highly perturbed. For this reason the trap identification is better done on a weakly populated system, while the global density is better measured on a fully saturated system.

- Optical filling and TSC spectrum-Influence of excitation wavelength :

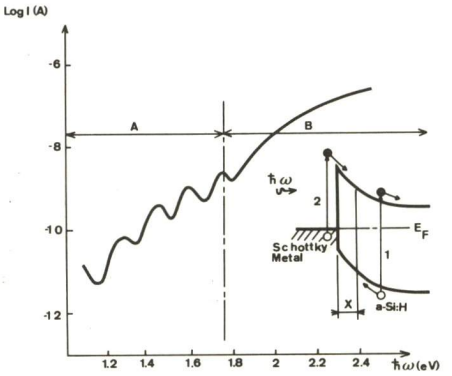

Fig.1 TYPICAL SPECTRAL RESPONSE OF Pt/a-Si:H

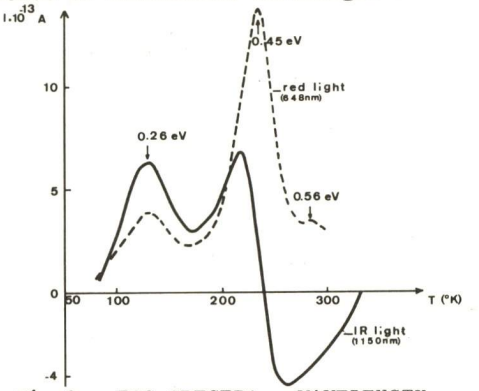

Fig.2 TSC SPECTRA : WAVELENGTH EXCITATION DEPENDENCE

Fig.1 shows the spectrum of photovoltaic I_{SC} typically obtained on a Schottky diode fabricated on a-Si:H. Two regions are clearly seen : A and B.

A : within this region where $\hbar\omega < Eg$ (optical gap) the current has the form:

$$I_{SC} = I_{Met} + I_{ph}, \quad (2)$$

where I_{Met} is the photoemission contribution from the metal toward the semiconductor. As shown in Fig. 1 (mechanism labeled 2) the electrons excited inside the metal are injected into the semiconductor whereas the holes are created on the spot. This current bears the following spectral distribution.

$I_{Met} \propto [\hbar\omega - \Phi_B]^2$ and gives the barrier height Φ_B together with other informations regarding the metal semiconductor interface [7]. I_{ph} is that contribution of the photovoltaic current which corresponds to the absorption tails. It follows approximatively an Urbach type law [9] and is the result of transitions from localized states towards the bands. This contribution which is indicative of "material quality" depends upon hole transport in the structure and is rapidly decreasing when temperature is lowered. This allows the measurement of Φ_B at low temperature on samples for which the state density within the gap is relatively important [9]. The structure which is seen on Fig.1 is due to interference effect.

B : In this part of the spectrum the photovoltaic current is due to the electron hole pairs created by interband transitions within the collection region. For photons having energies higher than 3.5 eV these pairs are created very close to the surface which allows the hole trap distribution of the structure to be analyzed.

Fig.2 shows TSC spectra which have been obtained after illumination at 77K by 2 eV and 1.08 eV photons respectively. For $\hbar\omega$ = 2 eV the absorption coefficient of the material amounts to 10^3 cm^{-1}, the trap filling is thus homogeneous and the TSC spectrum thus refers to the bulk traps both for electrons and holes. For $\hbar\omega$ = 1.08 eV ($\hbar\omega > \Phi_B$) carriers which cross the diode at 77K are at least partially electrons which come from the Schottky metal (internal photoemission). These electrons are thus not homogeneously generated in contrast with the preceding experiment and as a consequence most of them get trapped in the close vicinity of the Schottky electrode. The result is that the electron traps are rapidly filled up in the electrode vicinity and that the space charge region gets inverted there. The corresponding TSC spectrum (Fig.2 IR light curve) shows very specific features. It is composed at the same peaks as in the preceding experiment (at $\hbar\omega$ =2eV) but the relative intensity is modified and a negative part appears around 0.45 eV which probably corresponds to traps which are emptying within the inverted region of space charge.
For photons having energies higher than 2.5 eV α is greater than 10^5 cm^{-1} some samples have TSC spectrum with inverted intensity ratio of the peaks at 0.26 eV and .45 eV. This inversion might be due to some spatial distributions of trap density as well as to a gap distribution [7] within the structure.

Density of states :

It is assumed that :

i) the charges collected in the external circuit only come from the collection region [6] ;

ii) retrapping is negligible since local electrical field is of the order of 10^4 $V.cm^{-1}$.

An uniform density of electron-hole pairs is generated into the material by illuminating the structure during a time long enough to allow complete saturation as shown in Fig. 3. Trap concentration is simply determined by measuring the associated charge release Q_M.

$$Q_M = \int_o^t i_{TSC}\, dt = A\, N_t\, X \quad (3)$$

Where X is the width of collection region (lower than the space charge region width)
A=diode area, e=electron charge, N_t=trap concentration

By integrating i_{TSC} corresponding to the A curve (saturation condition) in Fig.3 we may evaluate the total density of states to 10^{18} cm^{-3} to be distributed between the two main peaks at .26 and .45 eV. The method does not enable us to measure shallow traps (E_T< 0.15 eV) neither deep traps (E_T> 0.8 eV).

Electrical filling :

Fig.4 shows a TSC spectrum obtained after direct biasing of a Schottky structure at 77K. The current intensity was about 10^{-11} Acm^{-2}. It is to be noticed that at this temperature, transport in delocalized states ($E_C - E_F$ = .5 eV) is quite negligible and occurs mainly via localized states by hopping near the Fermi level.

Levels below the Fermi level being filled by definition, we think that only electron traps above E_f are likely to be filled. The TSC spectrum of fig.4 reveals the presence of an electron trap near .22 eV from the conduction band. Optical filling does not enable us to see this peak which is concealed by a hole trap at .26 eV. Further we may notice that for some diodes [6] although there is a current at 77K it appears impossible to fill the electron trap. We deduce that the electron density of traps is very low. In each case, the hole density of the traps is ten to hundred times higher than the electron density. For materials in which electron traps are not seen, we measured drift mobility (μ_D) about 10^{-2} $cm^2.V^{-1}.s^{-1}$ and found a typical non Gaussian transient transport. Recently Wronski et al. [12] measured $\mu_D \simeq .9$ $cm^2.V^{-1}.s^{-1}$ for electrons in glow discharge samples and found well defined Gaussian transient transport. So we believe that low mobility of electron in our sputtered material could be due to :

i) shallow traps ; ii) the presence of a very thin microstructure that we have recently observed by electron microscopy. These structures could be responsible for the dispersive non Gaussian transport.

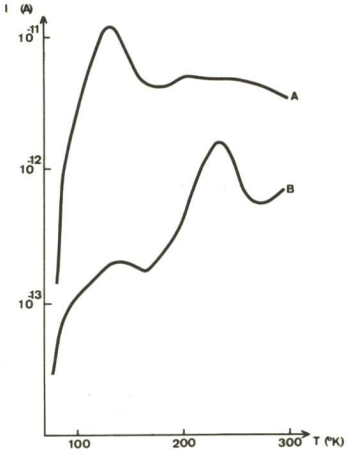

Fig.3 TSC SPECTRA : INFLUENCE OF THE EXCITATION TIME ($t_A > t_B$)

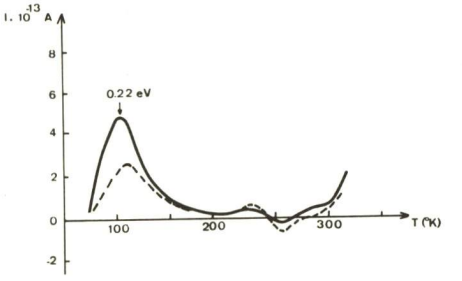

FIG.4 ELECTRICAL FILLING
- Solid line after biasing at 77K,
- Dotted line after biasing at 77K and IR emptying

Optical stimulation :

In addition to thermal stimulation, optical stimulation (OSC experiment) enables us to reach the "adiabatic" ionization energy of a filled state (i.e. without surrounding relaxation of ions or atoms). So from both experiments TSC and OSC we may deduce the amplitude of relaxation (Frank and Condon parameter) as well as the thermal and optical capture cross sections. For technical reasons we could only use a polychromatic IR light ($0.35 < \hbar\omega < 0.6$ eV), fig.4 shows the influence of such a radiation on a TSC spectrum (dotted curve is the TSC spectra after IR optical stimulation). The experiment consists in filling traps optically ($\hbar\omega \simeq 2$eV) or electrically, at 77K and in trying optically stimulated trap emptying by IR irradiation ($.35 < \hbar\omega < .6$ eV). Whatever the method of filling used we always observe at 77K during IR irradiation a photoionization current disappearing exponentially with time. We cannot yet conclude at this point on a possible lattice relaxation, but we can deduce from this experiment that the optical capture cross section for defects seen on TSC spectra is near 10^{-17} cm^2.

In conclusion these preliminary results show that a thermal and optical spectroscopy of defects can be undertaken successfully in a-Si:H. These methods complementarily with classical ones (field effect, capacitance and drift mobility measurements...) should enable us to obtained a better experimental knowledge of the physics of the states above the valence band, and the influence of microstructures on transport and electronic structures of this kind of material.

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