Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, pp. 531-534

# Invited

## Interface States in Amorphous Silicon/Amorhous Silicon Nitride Superlattice Structures

T. Tiedje, C. B. Roxlo, B. Abeles, C. R. Wronski

Corporate Research Science Laboratories Exxon Research and Engineering Co. Route 22 East, Clinton Township Annandale, New Jersey 08801, USA

The density of electronically active defect states has been determined in amorphous semiconductor superlattice structures consisting of alternating layers of a-Si:H and a-SiN<sub>x</sub>:H. Results obtained from dark conductivity, photoconductivity spectral response, electroabsorption and photoluminescence are discussed.

### 1. Introduction

It has recently been discovered that amorphous silicon (a-Si:H) and related materials can be grown in ultra-thin coherent layers only a few interatomic distances thick, both in the form of multilayered superlattice structures<sup>1</sup> and in individual double heterostructures.<sup>2</sup> This discovery has led to the observation of quantum size effects in amorphous semiconductors and holds promise for a variety of interesting scientific and technological applications for a new class of "ordered" amorphous materials. The electronic properties of the interfaces between the individual amorphous layers will be one of the most important factors in determining the value of amorphous semiconductor superlattice materials in electronic and electrooptic applications. In this paper we discuss what can be learned from recent transport and optical experiments about the nature of the interface states in a-Si:H/a-SiN<sub>x</sub>:H (silicon nitride) superlattice structures.

The superlattice materials were prepared by plasma assisted CVD at  $220^{\circ}$ C from pure silane and 1:5 SiH<sub>4</sub>/NH<sub>3</sub> mixtures, as discussed earlier.<sup>3</sup> The individual layers were obtained by changing the composition of the reactive gases in the deposition chamber without terminating the plasma. The gas exchange time, calculated from the pressure (30mT), flow rate

(100sccm) and volume of the deposition chamber, was about 1s, which is short compared with the time required to grow a monolayer (3-5s). In this paper we describe what has been learned about gap states associated with the a-SiN<sub>X</sub>:H layers from conductivity, photoconductivity (PC), electroabsorption (EA) and photoluminescence (PL) measurements on a series of a-Si:H/a-SiN<sub>X</sub>:H superlattice materials where the thickness  $L_N$  of the nitride layer was held fixed at 35A and the silicon layer was varied from  $L_S$ = 8A to 1200A.

#### 2. Conductivity

The in-plane resistivity of films deposited on quartz substrates is shown in Fig. 1 as a function of the total number a-Si:H sublayers M in the film, for a variety of different values of  $L_{S}$ . For a given value of  $L_{S}$  the resistivity decreases as the films become thicker (large M) to such an extent that the thick films are much more conductive (~  $10^3 \Omega$ cm) than bulk a-Si:H films prepared under the same conditions (~10<sup>8</sup>Ωcm) or even bulk a-Si:H films contaminated with 5% NH<sub>3</sub> in SiH<sub>4</sub> ( $\sim 10^{9} \Omega$ cm). The high conductivity of the thick layered films is due to a transfer doping effect in which the a-SiN<sub>x</sub>:H layers or their interfaces pin the Fermi level close to the a-Si:H conduction band.4

The decrease in resistivity with increasing



Fig. 1. In-plane resistivity as a function of the number of superlattice periods. The experimental points are for L<sub>S</sub> = 1200A ( $\neg$ ), 400A ( $\bigcirc$ ), 160A ( $\Box$ ), 80A ( $\diamondsuit$ ) and 40A ( $\triangle$ ).



Fig. 3. Excess absorption at 1.1 eV as a function of the number of layers per unit thickness of the film.



Fig. 2. Optical absorption spectra determined by photoconductivity for a layered film with  $L_S$  = 1200A and  $L_N$  = 35A compared with spectra for P doped and intrinsic a-Si:H films prepared under the same conditions.



Fig. 4. Electroabsorption signal for a sample with  $L_S$  = 20A and  $L_N$  = 35A and a photon energy of 1.94 eV. The inset is an expanded version of the horizontal intercept.

number of layers is due to a band-bending effect. In the simplest model of the bandbending, all of the charge in the depletion layer resides in the nitride or at the a-Si:H - a-SiN<sub>X</sub>:H interface. This assumption is consistent with the observed Fermi level pinning by the nitride. If the screening charge is uniformly distributed in energy, then the conductivity is given by, 4

$$\vec{\sigma}(M) = \frac{\vec{\sigma}_{o}}{M} \quad \underset{m=1}{\overset{M}{=}} \exp(-\frac{e\phi_{o}}{kT} \exp(-\frac{mL_{N}}{X_{N}} (L_{N} + \frac{\varepsilon_{N}}{\varepsilon_{S}} L_{S}))$$
(1)

where  $X_N = \sqrt{\epsilon_N/eN_{tN}}$  and  $N_{tN} L_N$  is the total screening charge per unit energy from each nitride layer. The solid lines in Fig. 1 are a best fit of Eq. (1) to the data with a bandbending  $\phi_0$  at the substrate interface of leV,  $\epsilon_N = 7.5$ ,  $\epsilon_S = 12$ ,  $\sigma_0 = 10^3 \, (cm)^{-1}$  and  $L_N N_{tN} = 2 \times 10^{11} \, cm^{-2} \, ev^{-1}$ .

3. Photoconductivity Spectral Response

The transfer doping produces material with lower defect densities than substitutionally doped material with comparable resistivity as is illustrated in Fig. 2. In this figure we show the photoconductivity (PC) response spectra for a homogeneous undoped a-Si:H film with resistivity  $\sim 10^8$  cm, a transfer doped film with L<sub>S</sub> = 1200A and resitivity  ${\sim}10^{3}_{\Omega}\text{cm},$  and a P doped film also with resitivity  $\sim 10^3$  cm. The PC spectral response at low photon energies, associated with defect states, is much smaller in the layered material than in the P doped material. The PC data was found to be consistent with photothermal deflection results.

Nevertheless the layered materials does have more defect state absorption than bulk a-Si:H prepared under the same conditions. This excess absorption is proportional to the number of a-SiN<sub>X</sub>:H layers as illustrated in Fig. 3. The line through the data in Fig. 3 corresponds to 1.4 x  $10^{11}$  states/cm<sup>2</sup>/eV/interface based on an assumed optical absorption crossection of  $10^{16}$  cm<sup>2</sup>.

### 4. Electroabsorption

Another quantity of interest, namely the net charge on the interfaces, can be measured by

the electroabsorption (EA) technique. This technique makes use of the fact that an electric field causes a transmitted light beam to be attenuated, proportional to the square of the applied field  $E = D/\underline{c}$  as follows:

$$\Delta \exists \neq \int_{0}^{d} \iota(x) \ K \ D^{2}(x) dx \qquad (2)$$

where K is an electro-optic coefficient, and  $\alpha(x)$  is the zero field absorption coefficient. The field inside the material contains contributions from the internal charge distribution plus an externally applied potential which has a d.c. component  $V_{\mbox{dc}}$  and an oscillatory component V<sub>ac</sub> cos wt. In the wavelength region where the a-SiN<sub>x</sub>:H layer is transparent and the a-Si:H absorbing, the EA signal at the frequency  $\omega$  is proportional to:

$$V_{ac} \left[M\phi_{S} - V_{dc} \left(1 + \frac{L_{N} \varepsilon_{s}}{L_{s} \varepsilon_{N}}\right)^{-1}\right]$$
 (3)

for a sample with M a-Si:H layers, each with a built-in potential across it of  $*_s$ .

An experimental EA signal plotted as a function of  $V_{dc}$  with  $V_{ac}$  as a parameter is shown in Fig. 4. The 36 V intercept is the built-in potential; which is clearly too large to be explained by Schottky barrier formation. From the data in Fig. 4, the sample thickness (1 $\mu$ m), and the a-Si:H layer thickness (20A) one can infer that the built-in potential per layer  $\phi_{e}$ is 0.05ev. The simplest charge distribution consistent with this internal potential is a positive charge of 2 x  $10^{12}$  electrons/cm<sup>2</sup> at the  $a-SiN_x$ :H-on-a-Si:H interface and an equal negative charge on the opposite interface. The assymmetry between the two interfaces has been attributed to strain-relieving defects analogous to misfit dislocations in crystalline heterojunctions.<sup>5</sup> The silicon layer thickness dependence of the EA signal (not discussed here) suggests that the charge distribution is more complex and that it extends into the a-Si:H layer.<sup>5</sup> However, midgap states in the a-Si:H layer. with the required density, are inconsistent with the absorption data in Fig. 3, an inconsistency which is not understood.

#### 5. Photoluminescence

The photoluminescence (PL) efficiency is also sensitive to the density of defect states. In Fig. 5 we show the PL efficiency at 10K for five samples with different  $L_S$  and for a bulk a-Si:H sample. The samples were deposited on smooth substrates, which leads to lower PL efficiency than rough substrates due to optical confinement effects. The PL efficiency in Fig. 5 shows no systematic variation with  $L_S$ , and is a factor of about 10 smaller in the layered materials than in the bulk a-Si:H.



Fig. 5. Photoluminescence efficiency as a function of a-Si:H layer thickness. efficiency for a bulk a-Si:H film is also shown.

The reduced PL efficiency in the layered materials is interpreted as evidence for electronically active defect states at the interfaces or in the a-SiN<sub>x</sub>:H layers accessible by tunnelling. By analogy with the quenching effect of dangling bonds on the PL in bulk a-Si:H,<sup>6</sup> we assume each defect state has a non-radiative capture radius R = 70A. Since  $L_S$ <40A in Fig. 5, the non-radiative capture process is two dimensional. In this case the PL is reduced by exp  $(-\pi R^2 N_{\varsigma})$  from the value it would have in the absence of the defects, where N<sub>S</sub> is the area density of the non-radiative centers. Setting the last expression equal to the experimentally observed reduction in PL intensity in the layered material we find that  $N_{\rm S} = 1.5 \times 10^{12} \, {\rm cm}^{-2}$ .

## 6. Discussion

The state densities determined by the

various techniques are summarized in Table I.

Table I	:	Interface	State	Densities	Per	Layer
Techniq	ue	(	J	PC	EA	PL
Density	(]	L0 <sup>12</sup> cm <sup>-2</sup> )	0.2	0.3	4	1.5

The thickness dependence of the conductivity  $(\sigma)$ and the PC response spectra both give values that are an order of magnitude smaller than the other two techniques. Possible explanations are as follows. The PC is only sensitive to states in the silicon layers, while the bulk of the states may actually be in the nitride. Secondly the state density inferred from the conductivity is ambiguous to the extent that the film may have also a depletion layer at the free surface in addition to the substrate interface, contrary the assumption in the analysis. This to modification of the model would increase the inferred density of states by a factor of about four and reduce the discrepancy with the EA data. Another possibility is that the internal fields are due to deep states close to the valence band that are not affected by bandbending.

The interface densities of states in Table I can also be expressed as bulk densities in the a-SiN<sub>x</sub>:H layer. The result ( $6 \times 10^{17}-10^{19} \text{cm}^{-3}$ ) is consistent with what is known about the density of gap states in silicon nitride. How the states are distributed between the bulk and the interfaces is not clear, although the asymmetry inherent in the EA results show that some modification of the density of states does occur at the interfaces.

#### References

- B. Abeles and T. Tiedje, Phys. Rev. Lett. 51, 2003 (1983).
- H. Munekata and H. Kukimoto, Japn. J. of Appl. Phys. <u>22</u>, L544 (1983).
- B. Abeles, et al., Proc. of Int. Top. Conf. on Transport and Defects in Amorphous Semiconductors, Bloomfield Hills, MI (1984).
- T. Tiedje and B. Abeles, Appl. Phys. Lett. (to be published).
- C. B. Roxlo, B. Abeles, T. Tiedje, Phys. Rev. Lett. <u>52</u>, 1994 (1984).
- B. A. Wilson, A. M. Sergent, J. P. Harbison Bull. Am. Phys. Soc. 29, 508 (1984).
- J. Robertson, M. J. Powell Appl. Phys. Lett. <u>44</u>, 415 (1984).

534