

## Analytical determination of the density-of-gap-states distribution in amorphous semiconductors: Experimental results

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The density of states in the mobility gap of amorphous silicon films has been determined by means of field-effect measurements. The samples were deposited by laser-induced chemical-vapor deposition. The analytical determination of the density-of-states distribution is based on the analytical solution of the Fredholm equation of the first kind relating the induced space-charge density and the density of states.

### I. INTRODUCTION

The knowledge of the density of states in the mobility gap of semiconductors with disordered structures is a fundamental aspect for understanding their electronic properties. Many techniques have been employed, but one of the most used is the field-effect technique.<sup>1-5</sup> However, this method has been subjected to criticism owing to its limitations.<sup>6</sup> Such limitations are mainly due to the presence of surface states at semiconductor-insulator interface, flat band potential determination, specimen homogeneity, and difficulties in computing the density of states from experimental field conductance. A detailed description of the field effect in amorphous films can be found in Ref. 1. The exact determination of  $N(E)$  requires the solution of a linear Fredholm integral equation of the first kind, which relates the density of space charge  $\rho(V)$  at the interface to  $N(E)$  itself. The computation of  $N(E)$  is based either on an iterative self-consistent method<sup>4,7</sup> or on a deconvolution procedure.<sup>8</sup> The former does not allow to define a unique  $N(E)$  from the experimental field-effect data and, consequently, to decide for the effective presence of peaks in the density-of-states distribution.<sup>4</sup> The computing procedure is time consuming and in order to get results in a reasonable time, a relatively big computer is necessary.

The deconvolution method<sup>8</sup> leads, generally, to a set of algebraic equations often ill-behaved. This originates solutions without physical meaning.<sup>9</sup> Recently, Augelli *et al.*<sup>10</sup> have solved the Fredholm integral equation. This was done assuming the space charge density as a polynomial function of the potential  $V$ ; the coefficients of this polynomial are strictly related to the density-of-states distribution.

In this paper we report on field-effect measurements and the density-of-states distribution computed by using the analytical solution reported in Ref. 10.

### II. ANALYTICAL SOLUTION

In this section, we will recall the main points of Ref. 10 for the benefit of the reader. The density of the space

charge at the insulator-semiconductor interface,  $\rho(V)$  is related to the density of states by the first type Fredholm integral equation:

$$\rho(V) = -e \int_{-\infty}^{+\infty} N(E)[f(E - eV) - f(E)]dE, \quad (1)$$

where  $e$  is the electronic charge,  $f(E)$  is the Fermi function, and  $V$  is the potential inside the semiconductor. With the positions  $y = \exp(eV/kT)$ ,  $a = \exp(-E_f/kT)$ , and  $z = \exp(E/kT)$ , being  $E_f$  the energy Fermi level in the semiconductor, it can be shown that Eq. (1) can be written as the following Stiltjes integral equation:

$$\frac{a}{e}(1 - ax')^{-1} \rho[kT \ln(ax')/e] = \int_0^{\infty} \frac{\omega(z)}{x' + z} dz \equiv \Phi(z), \quad (2)$$

where  $x' = y/a$ .

In Eq. (2),

$$\omega(z) = akTN[kT \ln(z)]/(az + 1) \quad (3)$$

is the inverse Stiltjes transform and the problem is now reduced to determine, if it exists,  $\omega(z)$ . It can be shown<sup>10</sup> that if one assumes that the space-charge density is a polynomial function of the potential  $V$ :

$$\rho(V) = a_1 V + a_2 V^2 + \dots + a_n V^n. \quad (4)$$

$\omega(z)$  exists and is given by

$$\omega(z) = \frac{a}{e} \sum_{m=1}^n A_m \omega_m(z), \quad (5)$$

where  $A_m = a_m (kT/e)^m$  ( $m = 1, 2, 3, \dots, n$ ) and

$$\omega_m(z) = \frac{1}{1+z} \sum_h (-1)^{(h+1)/2} \pi^{h-1} \left[ \begin{matrix} m \\ h \end{matrix} \right] (\ln z)^{m-h}$$

with  $h = 1, 3, 5, \dots$  (odd integer). In Eq. (4)  $n$  is an arbitrary integer.

Finally, inserting Eq. (5) in Eq. (3) we get the expression

$$N(kT \ln z) = \frac{az + 1}{ekT} \sum_{m=1}^n A_m \omega_m(z) \quad (6)$$

for the density of states. As the density of states is generally expressed as a function of the energy we can rewrite Eq. (6) assuming the Fermi level as the reference level for the energy, i.e.,  $E_f=0$ , and measuring  $V$  in eV. Then we obtain

$$N(E) = - \sum_{m=1}^n a_m (kT)^{m-1} \times \sum_h^m \left[ \frac{m}{h} \right] (-1)^{(h+1)/2} \pi^{h-1} \left[ \frac{E}{kT} \right]^{m-h} \quad (7)$$

### III. EXPERIMENTAL

Field-effect measurements were carried out on samples of amorphous silicon deposited by laser-induced chemical-vapor deposition (LICVD). The starting material was silane ( $\text{SiH}_4$ ) and argon was used as a carrier gas in the reaction chamber. Details on the deposition apparatus can be found elsewhere.<sup>11</sup> The substrate temperature was  $T=360^\circ\text{C}$  for sample 1 and  $T=380^\circ\text{C}$  for sample 2. The total pressure in the reactor was about  $1 \times 10^3$  Pa, while the silane pressure was  $5 \times 10^2$  Pa. The film thickness was  $0.7 \mu\text{m}$  and the optical gap was 1.8 eV in both samples. The films were deposited on aluminum ceramic substrates with a standard insulated-gate field-effect transistors (IGFET) configuration. A rectangular aluminum contact ( $0.5 \times 0.1 \text{ cm}^2$ ) was sputtered on the substrate. Sputtered on the metallic contact was an insulating layer ( $0.5 \mu\text{m}$  thick) of silicon nitride ( $\text{Si}_3\text{N}_4$ ), much larger than the Al contact. The silicon film was deposited on the insulating layer and, finally, two Al contacts, 0.1 cm apart, were sputtered on the outer surface of the silicon film. The inner Al contact was used as a "gate," while the other two as a "source" and "drain."

Field-effect measurements were carried out under the following conditions. (i) A constant voltage of 0.5 V was maintained between source and drain with a high stabilized power supply. (ii) A gate voltage,  $V_F$ , was applied between gate and ground, by means of a programmable power supply, and varied in the range  $-90$  to  $+70$  V. (iii) The field-effect current  $I$  was measured between drain and ground with a Keitley 619 electrometer. The sample was mounted in a cryostat and the measure was performed in a vacuum better than  $1.33 \times 10^{-4}$  Pa. The measure was fully controlled by a microcomputer HP86B. The computer controls the programmable power supply and increases  $V_F$  by steps of 0.3 V. A feedback control in the program verifies that  $V_F$  is at the correct value before reading  $I$ . In fact, a little voltage drift effect can be observed during the measurements, due to the time stability in the output of the power supply. Each experimental value of the field current  $I$  is averaged on one hundred readings (measure time about 10 s). Moreover, the first reading starts when the current changes for less than 1% during a time interval of 20 s. With this procedure one obtains the  $I$  versus  $V_F$  curve. Using the method proposed by Grünwald *et al.*,<sup>8</sup> it is now possible to calculate the charge density as a function of the potential at the

insulator-amorphous silicon interface. To perform this calculation, one needs the flat band potential  $V_{\text{FB}}$ . We determined  $V_{\text{FB}}$  with the conductance-voltage ( $G$ - $V$ ) characteristic at low  $V$  values and at a frequency of 20 Hz, and assuming as  $V_{\text{FB}}$ , the value of  $V_F$ , where the conductance curve begins to rise steeply.<sup>12</sup> For both specimens,  $V_{\text{FB}}=0.45$  V. As in Eq. (1) of Ref. 8 we need the current corresponding to  $V_F=V_{\text{FB}}$ ; the computer program allows firstly the measure of  $I=I_{\text{FB}}$ . After the calculation of the charge density, the computing procedure requires the determination of the polynomial function that best fits the calculated charge-density data. This part of the computing procedure is performed on a VAX 11/780 system using a MINUIT routine. The execution time varies from less than 1 min to about 10 min of CPU time, being longer for polynomials of higher degree. The coefficients of the best polynomial are then introduced in Eq. (7) to get, finally, the density of states,  $N(E)$ .

### IV. RESULTS

Figure 1 shows the field current  $I$  as a function of the gate voltage  $V_F$  for sample 2. A similar behavior has been obtained for sample 1. Dots represent the experimental values of the positive current for positive  $V_F$ , while triangles represent the absolute value of the negative current for negative external potential  $V_F$ . As one can see, the behavior is very similar for the two branches up to  $|V_F|=30$  V, while, for higher values, positive current increases rapidly and negative current tends to saturate. The field-effect response is bipolar and asymmetric, indicating that the insulator-semiconductor interface is slightly  $n$ -type.

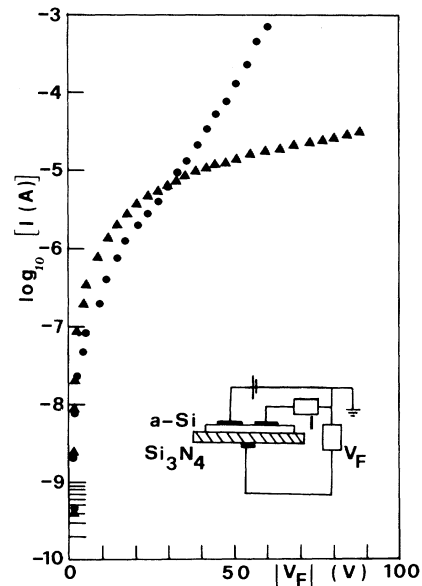


FIG. 1. Field current  $I$  as a function of the gate voltage  $V_F$  for sample 2. Dots and triangles are for positive and negative  $V_F$ , respectively. In the inset, a cross-sectional view of the insulated gate field-effect geometry is shown.

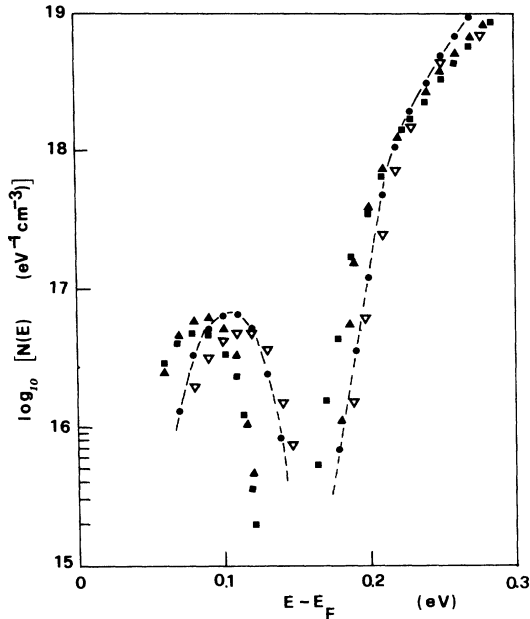


FIG. 2. Branch of the  $N(E)$  curve for positive values of  $V_F$  as computed for sample 1. The computing procedure used four polynomials of different degrees: (■) fifth, (▲) seventh, (●) ninth, and (▽) eleventh degree. The best fit is obtained with a ninth degree polynomial.

A portion of the density of states computed for sample 1 is shown in Fig. 2. In this case, we limited the gate voltage,  $V_F$ , between 0 and 15 V. This corresponds to an energy interval from near the Fermi level to about 0.3 eV from  $E_F$ , towards the conduction band. Behaviors of  $N(E)$  determined with four polynomials of different degree are reported. As one can see, the polynomials are all of odd degree. Actually, we tried to fit the space-charge-density data with polynomials of even degree, but the confidence level (CL) was always very low. The polynomial which better fits the  $\rho(E)$  curve is one of the ninth degree,

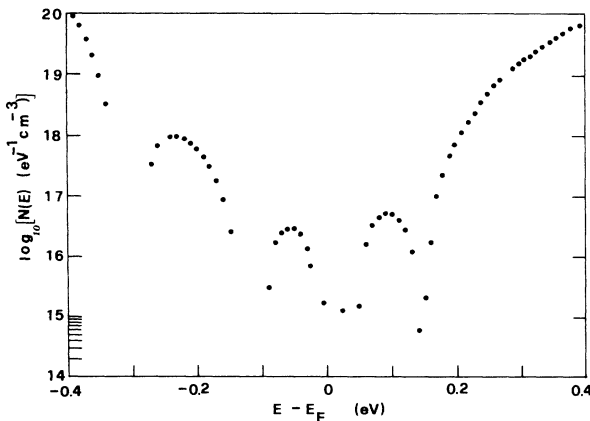


FIG. 3. Density of states computed for sample 2. The fitting procedure used a fourteenth degree polynomial on the whole ( $E - E_F$ ) considered range.

with a CL of 95%. Two major features can be evidenced from Fig. 2: (i) the density-of-states (DOS) distribution shows a well-defined peak at  $E - E_F \approx 0.1$  eV and (ii) the steep rise of  $N(E)$  in the energy range 0.15–0.30 eV. In fact,  $N(E)$  starting from about  $5 \times 10^{15} \text{ eV}^{-1} \text{ cm}^{-3}$  attains to  $10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$  at  $E - E_F \approx 0.3$  eV. Figure 3 shows the density of states,  $N(E)$ , for sample 2, in the energy range 0.4–+0.4 eV. We varied  $V_F$  in the range  $-90$  to  $+70$  V and consequently, the energy varied between  $-0.42$  and  $+0.54$  eV. The experimental measurements were performed with two different runs for negative and positive voltages. The positive branch is limited at 0.40 eV, because for values greater than  $+40$  V, the field current increases rapidly and we observed a heating effect in the sample.

We tried to fit all the positive and negative experimental points with a single polynomial. We were successful; in fact an eighth degree polynomial works, though with a low CL. The best result is obtained with a polynomial of fourteenth degree, which gives a CL of about 90%. In this case the degree of the polynomial is even, probably due to the symmetry of the curve. From Fig. 3 we can note the following. (i) The positive branch presents a well-defined peak at  $E \approx 0.1$  eV, followed by a minimum [ $N(E) \approx 5 \times 10^{14} \text{ eV}^{-1} \text{ cm}^{-3}$ ] at  $\sim 0.15$  eV. The difference between maximum and minimum is about 2 orders of magnitude. After such a minimum,  $N(E)$  begins to rise rather steeply and attains to  $8 \times 10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$  at 0.4 eV. (ii) For  $E < E_F$  the behavior of  $N(E)$  presents two peaks at  $\sim -0.05$  and  $\sim -0.22$  eV, respectively. At  $E = -0.4$  eV,  $N(E)$  attains to the value of  $2 \times 10^{20} \text{ eV}^{-1} \text{ cm}^{-3}$ . Similar results, for sample 2, have been obtained following a different best-fit procedure (Fig. 5). In Sec. V we will discuss and compare both approaches.

## V. DISCUSSION

The method used for the calculation of  $N(E)$  seems rather sensitive to fine structures, eventually present in the density of states distribution. The presence of these peaks is not a spurious effect, eventually due to experimental errors affecting  $I$  or  $V_F$ , but they should be considered as really present in the DOS distribution. The propagation of the experimental errors allowed to estimate an error of  $\pm 10\%$  on the space-charge-density values. Being that the errors on the coefficients of the polynomial very low, the error on  $N(E)$  data is practically the same like that affecting  $\rho(V)$  values. It can worthwhile be noted that rather different results can be obtained using PAIRED standard minimization routine running on a HP86B microcomputer and the MINUIT routine running on a VAX 11/780. An example is reported in Fig. 4, where the  $N(E)$  curves computed with a fifth degree polynomial are compared. The  $\chi^2$  test allows us to state that the  $N(E)$  curve computed by means of PAIRED routine is worse than that calculated by using a MINUIT routine. We can note that the  $N(E)$  behavior could also be obtained, using two polynomials of different degree for  $E > E_F$  and  $E < E_F$ . In Fig. 5 the  $N(E)$  behavior for sample 2 is obtained with a polynomial of the ninth degree for  $E > E_F$  and with a polynomial of thirteenth degree for  $E < E_F$ : both polynomials

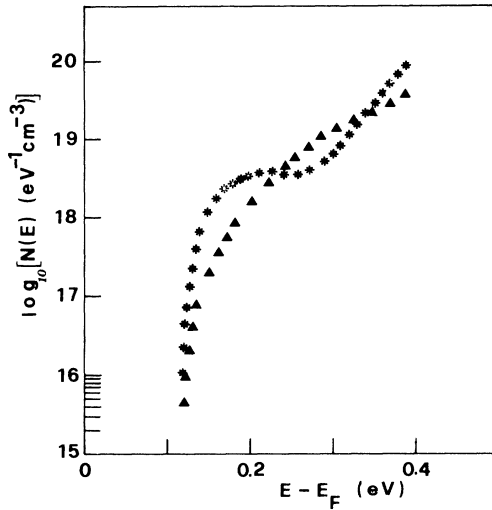


FIG. 4. Comparison between the  $N(E)$  results obtained using two fifth degree polynomials. The computations were performed with a MINUIT procedure running on a Digital Equipment Corporation VAX11/780 computer ( $\blacktriangle$ ) and with a PAIRED minimization routine running on a Hewlett-Packard HP86B microcomputer (\*).

give a CL of about 95%. This result can be compared with that presented in Fig. 3. As one can see, both behaviors are very similar, even if some slight shifts in the position of the peaks are observable. In order to decide which curve is better, we carried out measurements of the dark conductivity as a function of the temperature in the range 300–100 K on both samples. In sample 1, we found an activation energy,  $E_\sigma = 0.1$  eV which can be related to the peak in the  $N(E)$  curve (Fig. 2) located at  $E - E_F = 0.1$  eV.

For sample 2,  $E_\sigma$  was 0.10 eV, so that it seems more likely to associate such activation energy to the peak located at 0.10 eV in the curve presented in Fig. 3. It must be noted that in both cases (Figs. 3 and 5) the experimental values of  $I$  are taken with two separate runs, for positive and negative  $V_F$ . Before performing the second run, the sample was allowed to relax, until the field current  $I$  returned to the value measured at the beginning of the first run. We verified that this is sufficient to assure connection between the two branches of the curve. This is a fundamental point in order to perform the fitting of the space-charge-density data. However, we believe that it is better to fit the two parts of the  $I$  versus  $V_F$  curve by a

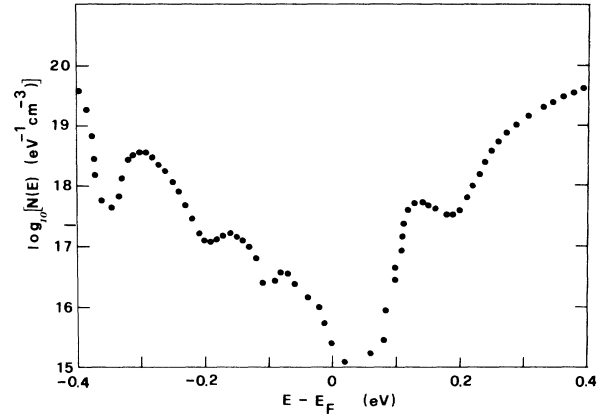


FIG. 5.  $N(E)$  distribution for sample 2 obtained with a polynomial of ninth degree for  $E > E_F$  and with a polynomial of thirteenth degree for  $E < E_F$ .

single polynomial. This is because the physical mechanism does not change going from negative to positive  $V_F$ . Finally, we notice the low value of the density of states near the Fermi level: for both samples it is about  $10^{15}$   $\text{eV}^{-1} \text{cm}^{-3}$ . This can be indicative that LICVD technique could be a useful method to deposit silicon films of good quality. The technique can be used for both undoped and doped samples.<sup>11</sup>

## VI. CONCLUSIONS

The density-of-states distribution in the mobility gap of amorphous silicon films has been determined by field-effect measurements, at room temperature. Following Grünwald *et al.*,<sup>8</sup> we were able to calculate the space-charge density  $\rho(V)$  at the interface insulator semiconductor. Such data were fitted by a polynomial function whose coefficients allow to calculate the density of states  $N(E)$  through Eq. (7). The investigated samples have a low density of states near the Fermi level ( $\sim 5 \times 10^{15}$   $\text{eV}^{-1} \text{cm}^{-3}$ ) and the peak appearing in the  $N(E)$  curves, above  $E_F$  can be related to the activation energy of the dark conductivity in the range 300–100 K.

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