CALCULATION OF BULK AND SURFACE ELECTRONIC PROPERTIES OF DIAMOND-LIKE SEMICONDUCTORS

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Local density of states (LDS) calculations have been performed by the recursion method for a model diamond-like semiconductor. LDS have been obtained for the following situations: the bulk, the vacancy and bivacancy in the bulk, the ideal (100) and (111) surfaces and the steps on these surfaces. Numerical results have been compared with experimental data for silicon. The calculated LDS show a one to one correspondence between the number of broken bonds on the investigated atom and the type of localized states near that atom. This supports the idea about the chemical nature of surface states, since the presence of steps on a strictly oriented surface leads to the appearance in the total density of surface states of additional peaks corresponding to another crystal surface.

Recent progress in experimental techniques made it possible to obtain for well defined surfaces (*e.g.* of silicon *etc.*) the density of electronic states[1], which is necessary for a correct understanding of the surface electronic structure and the nature of the surface chemical bond. Simultaneously with experimental investigations, also theoretical approaches marked a rapid development and among them especially the method of the empirical pseudopotential, the MSXα method, empirical tight binding methods and particularly the recursion method, the method of moments, the Bethe lattice method *etc.*[1,2]

In the present communication, LDS calculations have been carried our for an atom in the crystal bulk, near the vacancy and bivacancy in the bulk, on the ideal (111) and (100) surfaces and on several types of steps on these surfaces. The recursion method, introduced in 1972 by Haydock, Heine and Kelley[3], has been used in the calculations. Tight-binding parameters for the model diamond-like semiconductor, taken from ref.[4], have been non-zero for nearest neighbour interactions only.

RESULTS AND DISCUSSION

The recursion method consists of two stages. First, in finding the recursion coefficients a_i, b_i, $i = 1, 2, \ldots$ (coefficients of the tridiagonalized matrix of the hamiltonian); we have accurately determined the first fourteen coefficients which is equivalent to the consideration of fourteen coordination spheres, *i.e.* the effects of the reflection from the cluster boundary were absent. Second, in calculating LDS by means of the continued fraction; we have considered the infinite continued fraction by assuming that starting with $i = 15$, the coefficients a_i and b_i acquire constant values $a_\infty = 4$, $b_\infty = 5$ (eV), respectively, corresponding to the average values around which a_i, b_i oscillate for $i < 15$ (Fig. 1). The quantity b_∞ determines the width in the energy ($= 20$ eV), of the investigated region, while the quantity a_∞ determines the center of this region ($= 4$ eV, when $\varepsilon_s = 0$ is taken as the origin). Naturally, the best termination of the continued fraction in systems exhibiting energy gaps is a delicate mathematical problem[5]. Here, we have used the "constant coefficient" termination since it gave good results for the bulk LDS (Fig. 2).

Fig. 2 shows the results of the calculation of LDS on the atom in the crystal bulk. The LDS obtained is in good agreement with experimental UV-spectra[6] as well as the results of other calculations (Fig. 2 in ref.[7]). As seen from Fig. 2, the width of the valence band ($\cong 12$ eV) is well reproduced (the width of the forbidden band (gap) $\cong 1$ eV) and the same holds for the relative position of the characteristic peaks. The intensity of the peak near the bottom of the valence band is determined by *s*-states, the top of the valence band is formed by *p*-states and the bottom of the conduction band by *s*-states. This is in agreement with well known theoretical ideas on the character of hybridization in diamond-like lattices[8].

The formation of the vacancy or bivacancy by removing one or two atoms from the crystal bulk leads to the appearance of a localized state, the energy of which is located approximately in the middle of the gap (Fig. 3). This is in agreement with the experiment[9] and reflects the fact that crystal atoms close to the vacancy possess one broken bond each. Present calculations clarify the experimental fact of "healing" by hydrogen of defects in amorphous silicon[10]. Namely, the hydrogen atoms saturate the broken bonds of silicon atoms near the defects. In the present work, the above localized state is fourfold (or sixfold in the case of bivacancy) degenerate due to the absence of more distant interactions except between nearest neighbours. Were the former interactions also included, the degeneracy would have been lifted. Nevertheless, as it is well known from elsewhere (surface reconstruction)[11], degeneracy (or quasidegeneracy) of highest occuppied and lowest unoccuppied states leads to the appearance of Jahn–Teller (or pseudo Jahn–Teller) distorsions of the lattice. Such distortions are observed experimentally also around vacancies in diamond-like semiconductors[12].

Figs 4 and 5 present LDS calculated for atoms on ideal (111) and (100) surfaces, respectively.

Fig. 6 demonstrates the rapid change of LDS (*s*-states) during the transition from the (100) surface to the bulk. LDS for the bulk and the first two surface layers of atoms are presented. On the (111) surface, one peak of surface states is obtained whereas on the (100) surface, two surface state peaks appear near the gap edges.

It was in refs[13] that for the first time, the theory interpreting surface state existence as due to broken bonds, was elaborated[8]. An important consequence follows from

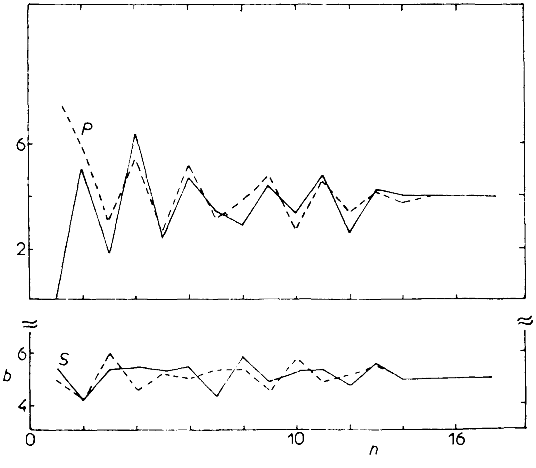


Fig. 1

"Oscillation" of a_n and b_n ($n = 1, 2, \ldots$) and the "constant coefficient" termination of the continued fraction for the situation of Fig. 2. ······ *s*-state, ------ *p*-state

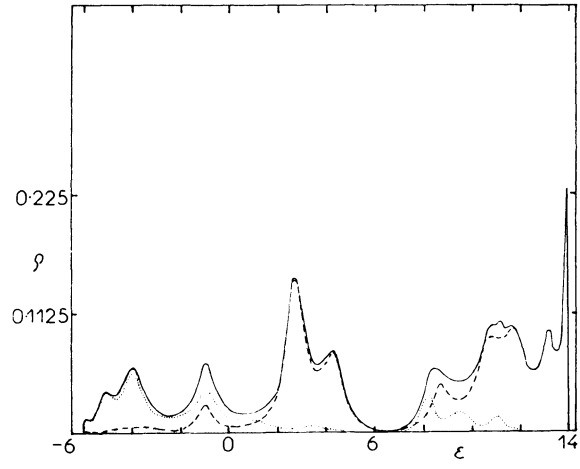


Fig. 2

Local density of states (ϱ) for the atoms in the bulk as a function of energy (ε). ······ *s*-state, ----- *p*-state, ——— total LDS this theory, namely, that the presence of steps on a strictly oriented surface should bring about the appearance of surface state bands untypical for that surface. To verify this proposition, calculations have been performed in the present work for several

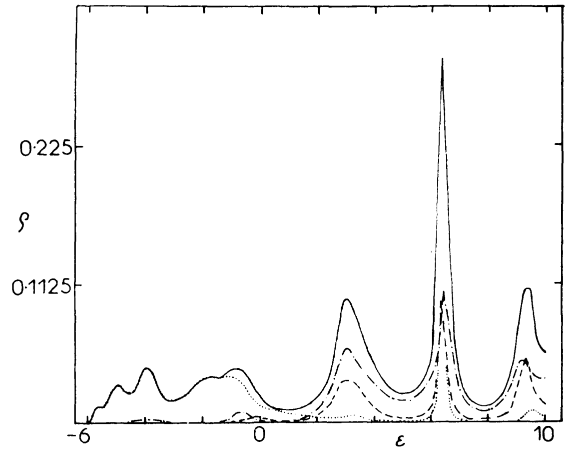


FIG. 3

Local density of states for the atom near the vacancy. ······· s-states, ----- $(p_x + p_y)$-states, -·-·-·- p_z-states, ——— total LDS; (z axis directed along the bond between two neighbouring atoms)

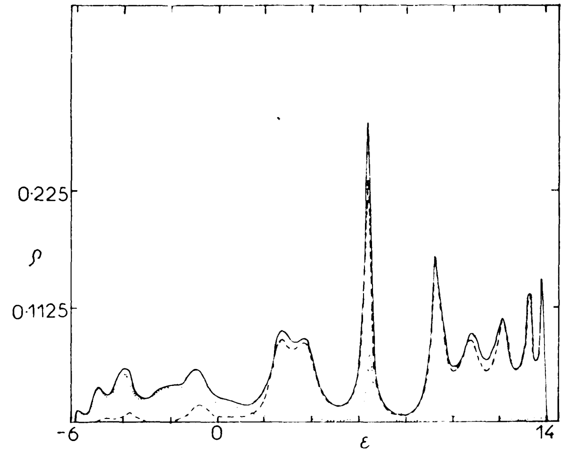


FIG. 4

Local density of states for the atom of the top layer on the (111) surface. Same notation as in Fig. 2

types of steps on the (111) and (100) surfaces. The examples of such a calculation can be found on Figs 7 and 8 where the investigated steps are also depicted. As seen

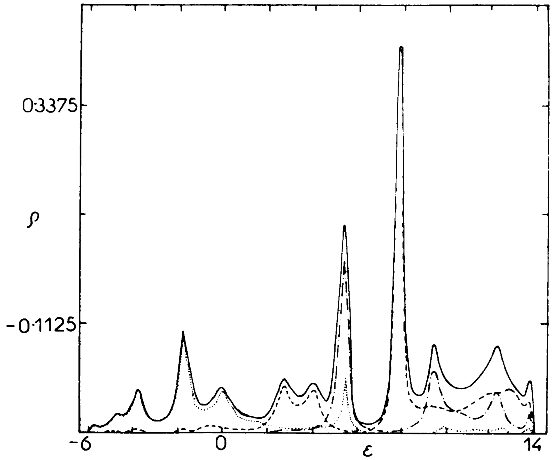


Fig. 5

Local density of states for the atom of the top layer on the (100) surface. ······· s-state, ----- $(p_x + p_y)$-state, -·-·-·- p_z-state, ——— total LDS; x, y and z axes directed along [100], [010] and [001] directions, respectively

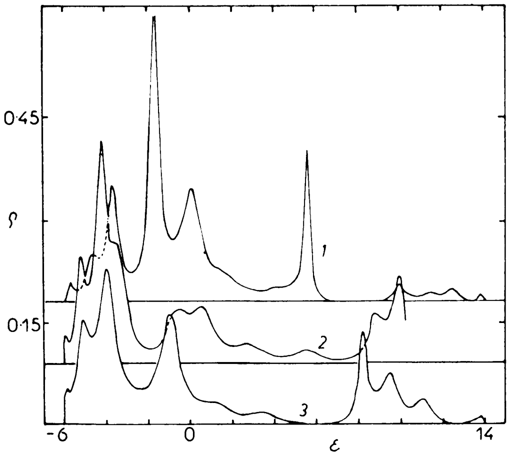


Fig. 6

Evolution of the LDS during the transition from the (100) surface into the crystal bulk for the s-states. *1* — 1^{st} layer atom, *2* — 2^{nd} layer atom, *3* — bulk atom from these figures, depending on the coordination of the atom A on the step, one or two bands of localized states show up which, according to their position on the energy scale, are analogous to surface state bands observed on ideal (111) and (100) surfaces[14].

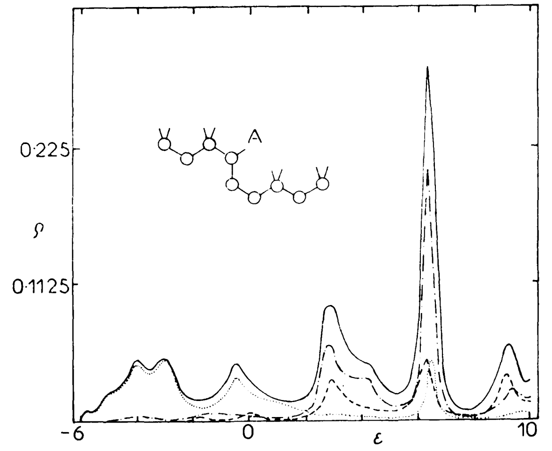
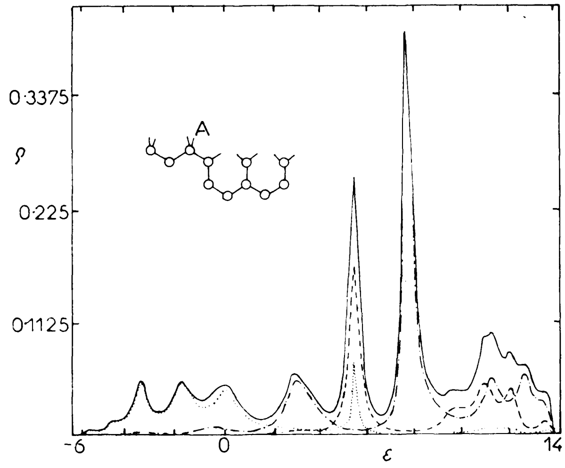


Fig. 7
Local density of states on atom A near the step on the (100) surface. Notation as in Fig. 5



Fig, 8
Local density of states on atom A on the step on the (100) surface. Notation as in Fig. 5

The results obtained testify to the efficiency of the recursion method for the calculation of LDS of finite crystals.

The calculations of steps proved the important qualitative feature of localized states on surfaces, namely, that owing to the chemical nature of surface states, the local character of the coordination of the atom determines the appearance and the number of surface state bands. This feature enables to predict qualitatively the surface state behaviour by considering local surface geometry independently from the character of the more distant surrounding.

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