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ELECTRONIC STRUCTURE OF a-Si3N4 : AB INITIO CLUSTER CALCULATIONS AND SOFT X-RAY EMISSION SPECTROSCOPY STUDY

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Partial local densities of states were calculated for silicon nitride clusters by ab initio self-consistent Hartree-Fock-Roothan method. The $=Si^0$ and $=N^0$ defects were simulated. In addition the nature of localized states of a-Si3N4 were studied by soft x-ray emission. Experimental and theoretical results are discussed.

1. INTRODUCTION

Amorphous silicon nitride (a-Si3N4) has excited great interest recently because of its various technological applications. The band structure has been investigated in some detail.[1,2]

The most correct calculations have been done by Ren and Ching[1] using the first principles LCAO method with a non-self consistent potential. The main results of this paper are: negligible small role of Si 3d- states in the valence band structure; the electronic structure of silicon nitride is defined by the short range order which is quite similar in all phases; the minimal basis set is sufficient to calculate the energy bands. The energy band structure of silicon nitride and its defects has been calculated by Robertson in references 2 and 3 by the non-self consistent tight-binding method. In these works, Si 3d wave functions were not included in the basis set. So up to now the self consistent calculations of silicon nitride's electronic structure have not been done. In the present paper, we try to fill the gap in this problem. In addition, x-ray emission was used to study the a-Si3N4 valence band states.

2. CALCULATIONS OF THE SILICON NITRIDE CLUSTERS' ELECTRONIC STUCTURE

The cluster calculations seem reasonable because the structure of a-Si3N4 is determined by short range order. The SiN4H8, SiN3H6, NSi3N9, NSi2H6 clusters were considered. Thus the $=Si^0$, $=N^0$ defects were simulated by SiN3H6 and NSi2N6 clusters. Hydrogen has a role of pseudoatoms for elimination of dangling bonds at cluster's borders. The Si-H and N-H bond lengths were taken to be 1.4800 and 1.0156 Å respectively. The cluster geometry

was determined according to information for the β-phase of silicon nitride that appears elsewhere.[4]

Partial local density of states (PLDOS) were calculated for silicon by ab initio self-consistent Hartree-Fock-Roothan method. The program HONDO-5 was used after its adaptation for a computer by A.A. Gorbik and A.S. Zjubin. The basis set includes 1s-, 2s-, 2p-, 3s-, 3p-, and 3d- orbitals of silicon; 1s-, 2s- and 2p- orbitals of nitrogen; and 1s- orbitals of hydrogen. Each basis function was set by a linear combination of Gauss functions. Thus for atomic orbitals (AO) of silicon and nitrogen, the (433/43/1*) and (43/4) representations were used respectively. for H the 1s-AO - STO-2G was used.[6] In the case of clusters with dangling bonds (the open shell system) the calculation has been done in the frame-work of the unrestricted Hartree-Fock method. The PLDOS of clusters was calculated with $\gamma^2 = 1 \text{ eV}^2$:

$$G_\alpha = \frac{1}{\sqrt{2\pi\gamma}} \sum_m A_\alpha^m \exp\left(-\frac{(E-E_m)^2}{2\gamma}\right)$$

where

$$A_\alpha^m = \sum_i \sum_{j,\beta} C_{i\alpha}^m S_{i\alpha,j\beta} C_{j\beta}^m$$

Here we are using routine notations.

3. EXPERIMENTAL TECHNIQUES

Amorphous silicon nitride films of 80 nm thickness were deposited on Si substrates by the CVD tetrachloride method. Silicon $L_{2,3}$ spectra were obtained by the direct method with a RSM-500 spectrometer-monochromator. The electron beam power was chosen taking into account the degradation of electronic structure of a-Si3N4 films

under the beam.[7] Thus it did not exceed 3 kVx1mA, which corresponds to an analysis depth of about 40 nm. The ratio of the maximum intensity of the Silicon $L_{2.3}$ band to the background intensity was greater than 10^3. With these conditions the NK_α spectrum intensity in the first order was smaller than that of $SiL_{2.3}$spectrum by a factor of 10^2.

4. RESULTS

Figure 1 depicts some calculated PLDOS and Silicon $L_{2.3}$ spectra of the VB (maxima A, B, and C) of the fundamental gap (maxima 1, 1'). There is a nearly complete absence of NK_α spectrum fourth order investment into silicon $L_{2.3}$ spectrum distortion in contrast to reference 8.

In the range of photon energy near 103 eV, i.e. 3.5 eV from the VB top (at 99.5eV) the complicated LS spectrum (maxima *l*, *l'*) was obtained as in references 9 and 10. Its nature - to our mind - is due to the occupied states in the fundamental gap of silicon nitride, cause by structural defects, perhaps Si-dangling bonds. Its location agrees well with the Fermi level position (1 eV from E_c). Such an interpretation permits one to understand a high sensitivity of the energy position and intensity of this spectrum to synthesis conditions, to appearance of Si-O bonds and to external factors, including: strong electric fields; UV-radiation; and fast electron radiation.[11] It is necessary to note that these LS are practically absent in Si K_β, N K_α spectra[9,10] giving the Si 3p, N 2p states distribution.

As is well known, x-ray emission spectra intensities I(E) in the one electron approximation are proportional to the matrix element of the electron transition probability, which results in the selection of states according to their symmetry, i.e. to the representation of PDOS of s-, p-, or d-symmetry in the corresponding emission band.

As seen in Figure 1, the calculated PDOS for the SiN_4H_8 cluster is well correlated with experimental silicon $L_{2.3}$ spectra and with Si K_β, N K_α spectra from reference 9. It is important to interpret silicon $L_{2.3}$ spectra with care. To do so, let us consider $G_{Si\ 3s} + G_{Si\ 3d}$ with $L_{2.3}$ spectra. Here the breaking of bonds leads to the appearance of occupied localized states in the fundamental gap. Maximum *l* is well distinguished in all PDOS for a

SiN_3H_6 cluster is of the highest intensity, although its value is smaller for example than corresponding maximum in $G_{Si\ 3s}(E)$ by a factor of two. Cluster simulation of the $=N^o$ defect shows that the N dangling bonds do not result in the appearance of local levels. This agrees with the results of reference 3.
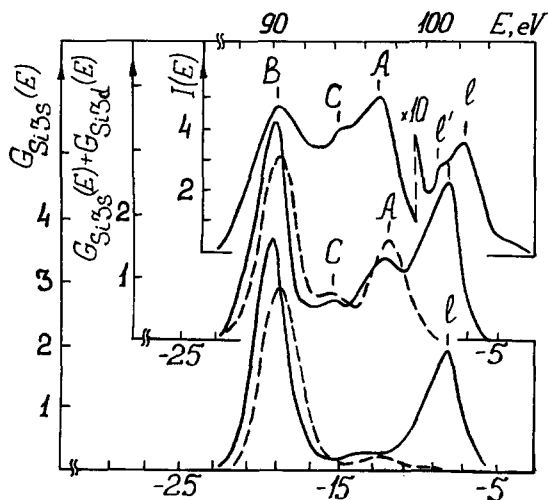

FIGURE 1
PLDOS of SiN_3H_6 cluster (------- spin "up", - - - - - - spin "down") and the silicon $L_{2.3}$ spectrum of a-Si₃N₄.

5. CONCLUSIONS

1. 3d-states play a major role in the formation of VB states. The neglect of these states[1-3] is not correct.

2. An occupied local level connected with Si dangling bonds arises in the fundamental gap.

3. The $=N^o$ defect does not result in the appearance of a local level.

4. The part of the silicon $L_{2.3}$ spectrum in the range of *l*, *l'* maxima is due to dangling bonds and perhaps to other defects in various charge centers.

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