Electronic structure of amorphous Si-N compounds

Electronic structure of amorphous Si–N compounds

M M Guraya†, H Ascolani†, G Zampieri†, J H Dias da Silva‡, M P Cantão‡ and J I Cisneros‡

† Centro Atómico Bariloche, 8400 Bariloche, Argentina
‡ IFGW, Universidad de Campinas, 13081 Campinas, Brazil

Abstract. We report results of experiments of valence band (VB) photoemission and dark conductivity of amorphous SiN_x:H ($0 \leqslant x < 1.5$). The most important change observed in the electronic structure when x increases is the replacement of Si–Si bonding states at the top of the VB by Si–N bonding states at the centre of the band. A plot of the band edges is presented which shows that the sudden opening of the gap at $x \simeq 1$ is due mainly to the recession of the conduction band minimum.

We have measured photoemission spectra of the valence band (VB) and the dark-conductivity of a-SiN$_x$:H compounds for compositions between $x = 0$ and $x = 1.35$.

The conductivity decreases with the N content x and, in the range 350–450 K, decreases exponentially with the inverse of the temperature. Assuming a $\sigma \sim e^{-E_a/kT}$ dependence we have obtained the activation energies E_a, which give the position of the Fermi level in the pseudo-gap relative to the conduction band minimum (CBM).

In the VB spectra taken at $h\nu = 1486.6$ eV two characteristic structures separated by a gap of ~ 4.5 eV are observed. One of these, a peak at ~ 20 eV which grows in intensity with the nitrogen content x, has almost exclusively N 2s character. The other structure, the upper part of the VB (between 0–15 eV), comprises the Si 3s, Si 3p, and N 2p contributions. At this photon energy the upper VB has maximum intensity at the bottom of the band, and this maximum shifts towards higher binding energies when x increases, closing the gap between the two structures. It can be shown that this maximum corresponds to the Si 3s partial DOS, which becomes enhanced at this photon energy.

Figure 1 shows the VB spectra taken at $h\nu = 151.4$ eV. Only the upper VB is shown because a spurious line of the Zr anode (C-K$_\alpha$, $h\nu = 278$ eV) produced a broad peak of Si-2s photoelectrons at the energies where the N 2s structure should appear. The most important change seen in the spectra when x increases is the shift of spectral weight from near the valence band maximum (VBM) towards the centre of the band. We have assigned the feature labelled A, prominent at low x, to the band of Si–Si bonding states, and the feature labelled C, which dominates at the near stoichiometric composition, to the band of Si–N bonding states. As expected, the band corresponding to the heteropolar Si–N bonds lies at higher binding energies than the band corresponding to the homopolar Si–Si bonds. The energy separation between the maxima of these bands is 5.7 eV. The feature labelled B is thought to have contributions from the Si–Si bonding states and from the N 2p non-bonding states.

Combining the determination of the VBM from the photoemission experiments with the optical gaps and activation energies we have constructed the diagram of the band edges and Fermi level positions shown in figure 2. Starting with the positions of the VBM relative to the Ar 2p$_{3/2}$ level (taken as a common reference level) we have added the optical gaps (Guraya *et al* 1990) to obtain the CBM and from these we have subtracted the activation
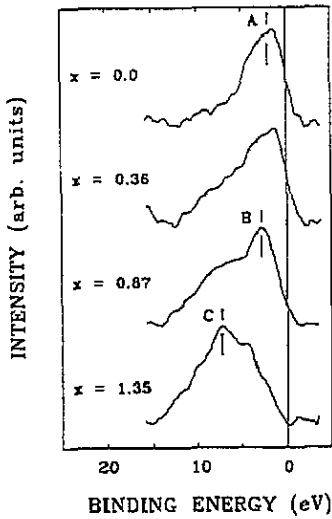
Figure 1. Valence band spectra with $h\nu = 151.4\,eV$. All the energies are referred to the Ar $2p_{3/2}$ level to which we have assigned a binding energy of 242.0 eV.
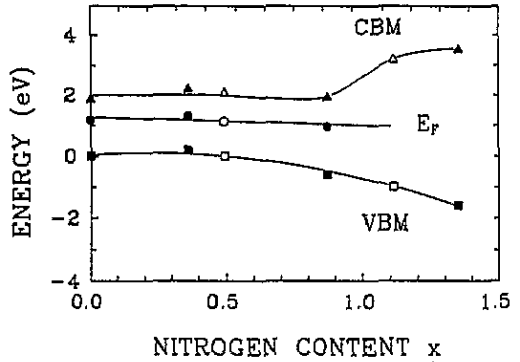
Figure 2. Band edges as a function of the nitrogen content. We have assigned $E = 0$ to the VBM of a-Si:H and we have referred all the energies to the Ar $2p_{3/2}$ level.

energies to obtain the Fermi level positions. The full curve in the figure is obtained from a quadratic fit to the VBM at $x = 0.0$, 0.36, 0.87, and 1.35, which has been used to locate the VBM of the samples with $x = 0.89$ and 1.11 (not measured) and then the CBM and Fermi level positions. It is seen that the sudden opening of the gap at $x \sim 1$ is due mainly to the recession of the CBM, the recession of the VBM being comparatively smaller. This is consistent with the picture that in the conduction band the Si–Si antibonding states are replaced by Si–N antibonding states, whereas in the top of the valence band the Si–Si bonding states are replaced by the N $2p$ non-bonding states, which lie above the band of Si–N bonding states.

To compare theory (Ordejon and Ynduráin 1991) and experiment one has to construct a theoretical photoemission spectrum by summing the calculated partial DOS weighted with the photoemission cross sections of the atomic orbitals, and convolute the theoretical spectrum with a Gaussian representing the experimental resolution. At $h\nu = 151.4\,eV$ the photoemission spectra resembles the DOS of the system because of similarity of the photoemission cross sections of the atomic orbitals involved.

Comparison of theoretical and experimental spectra shows a good agreement in the shape of the bands for all the compositions in both cases ($h\nu = 151.4\,eV$ and $h\nu = 1486.6\,eV$), although the theoretical spectra are too wide. A more detailed discussion will appear (Guraya *et al* 1992).

References

Guraya M M *et al* 1990 *Phys. Rev.* B **42** 5677
Guraya M M *et al* 1992 to be published
Ordejón P and Ynduráin F 1991 *J. Non-Cryst. Solids* **137** 891