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DISORDER EFFECTS ON GaP CORE LEVELS STUDIED BY ELECTRON SPECTROSCOPIES

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Abstract. - A study by X-ray induced photoelectron and Auger electron spectroscopies of P and Ga core levels from flash-evaporated crystalline and amorphous GaP films is presented. Beside the effects of contamination the results indicate the existence of partial chemical disorder in the amorphous material.

The existence of bonds between like atoms in amorphous films of the semiconductor compound GaP prepared by flash-evaporation has been inferred from several experimental data: optical and transport measurements (1) EXAFS (2) and soft X-ray spectroscopy results (3). As core levels binding energies are sensitive to the charge distribution around the atom, modifications of P and Ga photoelectron (XPS) and Auger spectra are expected when going from crystalline to amorphous GaP due to the presence of Ga-Ga or P-P bonds in the amorphous samples. However earlier investigations on core levels by photoemission for amorphous and crystalline GaP prepared by sputtering did not give evidence for wrong bonds (4) without excluding the presence of 5-10% of such bonds (5).

We present in this paper a comparative study of P and Ga core levels from amorphous and crystalline flash-evaporated GaP films by both photoelectron and Auger spectroscopies.

Experiments. - The samples were thin layers deposited by flash evaporation of crystalline powder under ultra high vacuum on Mo substrates maintained at room temperature. The crystalline film was obtained by in situ vacuum annealing at 550°C. The samples were stoichiometric within a few % as controlled by back scattering. The transfer into the electron spectrometer was made under dry air. The electron spectra, induced by the radiation emitted from an Al anode bombarded by 12 keV electrons, were recorded by means of an electrostatic hemispherical analyser operated at a resolution of 7.10⁻⁴. Under our experimental conditions, the sampled depth is estimated to be about 10 to 50 Å. The shift due to charging effect was taken into account by measuring all the peaks relative to C 1s which energy referred to the Fermi level was taken as 285.1 eV (6). Grazing-incidence X-ray reflectometry and spectroscopic ellipsometry results both showed the presence of a superficial oxide layer on amorphous GaP films. This layer was about 16 Å thick and had a very low average electronic density; moreover the interface with unoxidised amorphous GaP was probably complex. However, the nature of the layer was impossible to determine from these experiments (7). Contamination (C and O) was too high to obtain any valuable information about the valence band states but low enough not to alter the core level spectra significantly, as we shall see.

Results. - Fig.1 shows the Ga L₃ M₄,5 M₄,5 Auger electron spectra from amorphous and crystalline GaP. As reported by G. Shön (6), the L₃ M₄,5 M₄,5 Auger signal from metallic Ga consists in two main components separated by 3.7 eV; in Ga₂O₃ they are shifted by 5.7 eV towards lower kinetic
energies. For crystalline GaP, the Auger signal is similar to the pure Ga one but shifted by 2.6 eV towards lower kinetic energies. The additional structure observed on the spectrum for amorphous GaP can be attributed to Ga$_2$O$_3$ according to Shin values. This result indicates that only the amorphous sample contains a non negligible proportion of oxide.

Beside this contamination effect, a + 0.8 eV shift in kinetic energy is observed between the Auger signals of a-GaP and c-GaP. This shift cannot be attributed to the presence of Ga$_2$O$_3$, whose contribution at the relevant energies is very low. As it occurs towards the pure Ga signal, we can interpret this shift by the presence of Ga-Ga bonds in the amorphous sample.

The binding energies of Ga and P core levels deduced from XPS spectra are given in Table 1. The Ga and Ga$_2$O$_3$ corresponding energies, measured by Shin (6) are also reported. The precision on the absolute values is ± 0.2 eV but the shifts can be estimated within ± 0.1 eV.

The presence of Ga$_2$O$_3$ on the amorphous sample, as revealed by the Auger spectrum, is responsible for the spreading towards higher binding energies of the lines observed when going from c-GaP to a-GaP (fig. 2 shows the Ga 3d line). Besides this contamination effect, a systematic shift of the peaks is observed towards lower binding energies. The values of this shift is almost constant (0.2 eV) and occurs towards the position of the pure Ga line (the apparent higher shift of the 3p$_{1/2}$ line is an artefact due to the lack of resolution of the 3p doublet in a-GaP). This result argues again in favour of the existence of Ga-Ga bonds in the amorphous samples of GaP.

<table>
<thead>
<tr>
<th></th>
<th>c-GaP</th>
<th>a-GaP</th>
<th>Ga(6)</th>
<th>Ga$_2$O$_3$(6)</th>
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<tr>
<td>Ga</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2p 3/2</td>
<td>1117.5</td>
<td>1117.3</td>
<td>1116.3</td>
<td>1118.1</td>
</tr>
<tr>
<td>3s</td>
<td>160.1</td>
<td>159.9</td>
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<tr>
<td>3p 1/2</td>
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<td>107.6</td>
<td>106.9</td>
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<tr>
<td>3p 3/2</td>
<td>104.8</td>
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<tr>
<td>3d</td>
<td>19.5</td>
<td>19.2</td>
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<tr>
<td>P</td>
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</tr>
<tr>
<td>2s</td>
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<td>186.6</td>
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</tr>
<tr>
<td>2p</td>
<td>129.1</td>
<td>129.1</td>
<td></td>
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</table>

Table 1.- Binding energies in eV referred to the Fermi level (see text)
Moreover, the almost equal shift of the 2p and 3d levels explains why the atomic X-ray emission line Ga Kα (3d → 2p_{3/2}) was found identical in position in the crystalline and amorphous GaP forms (3).

The mean position of the 2s and 2p lines of phosphorus are not affected by disorder, within the limits of experimental error. The P 2p line is shown figure 3. P 2p lines from oxidized phosphorus, situated beyond 133 eV (8) have a negligible contribution to our spectra and cannot perturb the shape and the width of the observed lines. A nearly symmetric broadening of the 2s and 2p lines is observed for the amorphous sample. The absence of any shift of the P lines is difficult to explain if a certain degree of chemical disorder exists in the samples, as suggested by the behaviour of the Ga lines, unless the corresponding lines for pure P are very close to the lines for the compound. The presence of P-P bonds is on the other hand consistent with a broadening of these lines.

In conclusion, although the core level photoemission and Auger spectra show evidence for contamination effects, a comparison between the results obtained on amorphous and crystalline GaP samples prepared by flash-evaporation clearly indicates the existence of partial chemical disorder in the amorphous case. The photoemission and Auger Ga lines are shifted towards the pure Ga lines, suggesting the presence of an appreciable proportion of Ga-Ga bonds. The photoemission P lines on the contrary are not shifted but slightly broadened, therefore the evidence for P-P bonds is less clear. The present results confirm those already obtained by other experiments on similar samples. They are
however in contradiction with those obtained on sputtered amorphous GaP samples (4), which showed no evidence for chemical disorder. This may just reflect differences in the structure of the two types of samples prepared by different methods.

References

   Stirling. 1980.