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INITIAL STAGES OF GaP (110) OXIDATION

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We report preliminary data on oxygen chemisorption onto GaP(110),
obtained by photoemission with synchrotron radiation at the Grasshopper beam line of the Adone storage ring in Frascati. Clean surfaces from n-type single crystals (n=2x10^17) were prepared by cleavage in UHV. Core levels of both Ga(3d) and P(2p) as well as the valence band (VB) were investigated at increasing oxygen exposure. Fig. 1 shows the evolution of the VB for increasing oxygen coverages, while the Fermi level position relative to the linearly extrapolated VB edge is reported in Fig. 2.

Fig. 1 - Valence band for increasing O2 exposure.

Fig. 2 - Fermi level vs O2 exposure.
After cleavage, the Fermi level is 1.5 eV above the VB edge so that the initial band bending amounts to 0.5 eV. Two stages are observed in GaP (110) oxidation, at one monolayer regime. At low oxygen exposure (less than 10^3 L) a band bending increase up to 0.8 eV takes place, in agreement with results obtained by Sebenne et al. (1). At this stage the surface is still almost clean, in the sense that no major changes in the VB photoemission spectra are observed, as shown in Fig. 1. We estimate that this first oxidation stage corresponds to a surface coverage of the order of 10^-3 to 10^-2. Formation of extrinsic surface states due to oxygen bonding to special chemisorption sites, like cleavage defects, provides the most natural explanation of the observed band bending change. Also in GaAs(110) the initial oxygen chemisorption takes place on special sites and is cleavage dependent (2,3). The second oxidation stage consists in a gradual disappearing of intrinsic surface states due to oxygen interaction with dangling bonds. During this stage, between 10^3 L and 10^6 L approximately, the band bending is stationary. The subsequent oxidation induces major modifications of the VB spectra, owing to the increase of the oxygen photoemission peak. At the same time also the core level lineshapes exhibit changes due to chemical shift. For these reasons, at exposure larger than 10^6 L, band bending determinations based on either VB edges or core level positions are questionable. The data of Fig. 2 essentially agree with results obtained on GaAs(110) (2,4), showing initially a strong band bending change upon small oxygen exposure, followed by a plateau during the subsequent oxidation. Moreover the present data confirm the interpretation of recent optical results on both GaAs(110) and GaP(110) (5), in which Franz-Keldysh effect near the surface was observed in differential reflectivity upon oxidation. Fig. 3 shows a set of Ga and P core levels at increasing oxygen exposure. A well pronounced chemical shift is only visible for P (2p) at large exposure, while minor lineshape changes occurring at lower exposure cannot be unambiguously resolved with the present resolution. An intriguing feature present in the core level spectra is a marked broadening of the lineshapes (almost 0.5 eV) which seems to be correlated with the strong band bending increase between 10^3 L and 10^6 L. The origin of the broadening is not clearly understood yet. Similar effects, although not so large, have been some times observed in photoemission spectroscopy (2,6). They have been usually interpreted as due to inhomogeneous band bending at the surface (7).

We should also mention that most of the above described experimental observations regarding oxygen chemisorption onto GaP(110), including the amount of band bending change, the rate of oxygen uptake and the broadening in core level spectra are strongly dependent upon the quality of the cleave. The above reported data have been obtained on a very good cleave, while bad cleaves showed fairly different results. In particular the band bending change upon oxidation was much smaller, no broadening was observed and the rate of oxygen uptake was almost two orders of magnitude higher. The latter finding suggests a high density of steps in the cleaved surface. The above results are than consistent with the presence,
in bad cleaves, of step-related extrinsic states competing with oxygen induced chemisorption states in pinning the Fermi level. Further experimental work in progress in order to firmly establish the relevance of intrinsic versus extrinsic effects in GaP(110) oxidation.

Fig. 3 - Ga(3d) and P(2p) core levels for increasing $O_2$ exposure.

References:

(6) R.H.Williams, private communication.