[4] A. De Rújula, H. Georgi, and S. L. Glashow, Phys. Rev. D 12, 147 (1975).

[5] See Lane and Eichten, Ref. 3.

[6] The D^{0**} meson is assumed here to be a $^3P_1$ state.

[7] N. Cabibbo and R. Gatto, Phys. Rev. 124, 1577 (1961).

[8] Some data are available at $\sqrt{s} = 4.1$ GeV, but they are not statistically sufficient to plot the recoil mass spectrum.

Oxidation Properties of GaAs (110) Surfaces*

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If the cleaved (110) surface of GaAs is exposed to oxygen in its molecular ground state (exposures of 10^{12} Torr), oxygen is chemisorbed only on the surface As atoms and there is no breaking of bonds between the surface atoms (Ga or As) and the rest of the crystal. However, if the oxygen is excited, e.g., by an ionization gauge, these bonds are broken and oxidation proceeds past the chemisorption stage. The GaSb (110) surface behaves differently and will be discussed for comparison.

The use of synchrotron radiation in the range 10 to 300 eV allows one to examine the valence and core states of the last few atomic layers of many solids and to study sorption of gases in a very detailed manner. In a previous Letter,[1] studies of the oxidation of the GaAs (110) surface were reported where oxygen is adsorbed preferentially on the As surface sites. Here we report further studies which confirm and clarify that conclusion, but also, for the first time, show how the effect of oxygen can depend on whether or not the oxygen is in its molecular ground state. Furthermore, through chemical-shift data,[2,3] it is shown definitively that the difference is not only in order-of-magnitude increases in the rate of oxygen uptake but also in a change in the very nature of the oxygen sorption itself. Finally, lest these results be generalized to too great an extent, we note that the situation is quite different for exposure of the GaSb (110) surface to molecular oxygen in the ground state.[2]

In 1965, Archer and Gobeli[4] reported for cleaved (111) Si surfaces an increase in sticking coefficient of about a factor of 6 due to oxygen sorption with an ionization gauge in operation. However, in their experiments, a vac-ion pump was used during the oxygen exposure. This pump could have served as a source of excitation[5] for the oxygen. As the work to be presented here shows, oxygen uptake is much more sensitive to such excitation than has generally been realized in the past.

More recently, the effect of an electron beam during Auger measurements of oxygen sorption on Si has been noted,[6] and other related work on Si,[7-10] Ge,[9,11,12] and III-V compounds[10,13] has been reported. Here we want to note particularly the work of Ibach *et al.*[6] and Dorn, Lüth, and Russell[14] since their work provided the starting point for our original studies.[1] In the work of Ibach *et al.*,[6] it was implied that the effect of the ion gauge was removed by encasing it in a bent tube attached to the chamber, in order to ensure that no light, ions, or otherwise excited oxygen molecules could pass from the filament to the crystal without being scattered several times by the chamber walls. The same precautions appear to have been followed by Dorn, Lüth, and Russell[14] and were followed by us in our original work. Although the details of the geometry were different, we insured that several scattering events must take place between the ion gauge and the crystal under study. The rate of oxygen uptake found in these original experiments was in reasonable agreement with that of Ref. 14, i.e., a half-monolayer was formed at about 10^6–10^7 L after which the sorption rate decreased very strongly. As the results reported here show, under these conditions there is still an enormous effect from the ion gauge. By taking more stringent precautions to remove any effect of oxygen excitation, the exposure required for half-monolayer coverage is increased by several orders of magnitude. Furthermore, the nature of the oxygen sorption at high exposures is changed.

The photoemission measurements were done using synchrotron radiation in the same manner as reported earlier.[1] The samples were cleaved *in situ* in the ultrahigh vacuum chamber, 10^{-11} Torr, and then exposed to O_2 in a controlled way with the ion pump valved off and with no hot filaments, *e*-beams, etc., turned on. Up to 10^{-5}

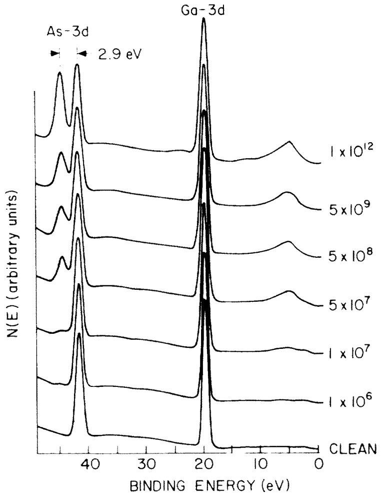

FIG. 1. Photoemission spectra ($h\nu = 100$ eV) of clean GaAs (110) and the same surface exposed to the indicted quantity of O_2 in the ground state. (1 L $= 10^{-6}$ Torr sec) Only chemisorption to the surface As atoms is observed.

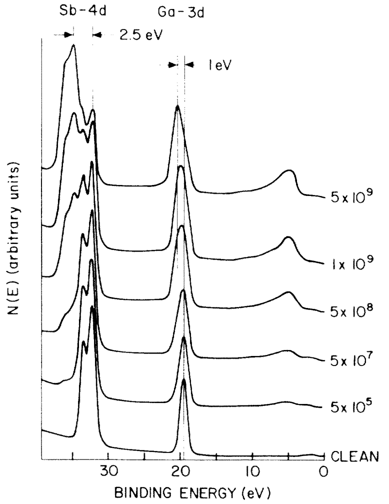

FIG. 2. Photoemission spectra ($h\nu = 100$ eV) of clean and oxidized GaSb (110). As for the data of Fig. 1, only O_2 in the ground state was used; however, oxidation goes beyond the chemisorption stage.

Torr, the O_2 partial pressure was measured with a cold-cathode device, located in a side arm ~ 20 cm from the sample and well out of the line of sight. A milliTorr gauge, located ~ 1 m from the sample by several bent tubes, was used in the pressure range 10^{-6}–10^{-1} Torr. A thermocouple gauge was used for pressures between 1–20 mmHg and a mechanical pressure gauge was used above 20 mmHg. By observing these precautions in measuring the pressure, we were able to remove all detectable effects of excited oxygen from the experiment, as will be discussed below.

The results of Fig. 1, when compared to those of Fig. 1 of Ref. 1, illustrate the differences in oxygen sorption obtained when sufficient precautions are taken to reduce the effect of oxygen excitation. As mentioned earlier, two very large differences are observed. First, the exposure for half-monolayer coverage is increased from 10^7 L to over 10^{11} L exposure; second, there is only one shifted As $3d$ peak ($\Delta E = 2.9$ eV) and there is no shift of the Ga $3d$ peak (although there is an increase of 0.5 eV in the width, full width at half-maximum, of the Ga peak after 10^{12} L exposure). In contrast, in the prior experiment, the single 2.9-eV As shifted peak was observed at 10^5 L with no Ga shift; however, at higher oxygen exposures ($\geq 5 \times 10^5$ L) another As peak shifted by 4.5 eV is observed as well as a Ga peak shifted by about 1.0 eV. Thus, it is clear that even when the ion gauge is out of the line of sight of the sample, very strong effects can still take place due to excited oxygen. Recognizing these effects, it is now clear that all prior work must be re-examined. For example, in the landmark work of Archer and Gobeli[4] the vac-ion pump was neither turned off nor valved off during the oxygen exposure; and, with regard to the work of Ibach *et al.*,[6] it is now clear that it is possible that oxygen excitation affected the results even when the ion gauge was out of the line of sight of the Si crystal. However, as will be shown presently, the effects of excited oxygen can also vary strongly from material to material.

The results of Fig. 1 confirm and greatly strengthen our conclusions concerning the preferential chemisorption of oxygen on the As surface atoms of the (110) GaAs crystal. In particular, they show that such an attachment takes place only as long as excited oxygen is not present. Clearly, the excited oxygen is capable of breaking bonds between the surface atoms and the rest of the crystal and only under these conditions will the Ga be oxidized and true oxides of Ga and As will be formed (as opposed to chemisorption of oxygen on a surface As atom which is properly bonded to the rest of the GaAs crystal).

As a comparison to our GaAs (110) data, we present in Fig. 2 our results for the GaSb (110) surface, prepared under the same experimental conditions as the GaAs sample of Fig. 1. The oxidation behavior of GaSb (110) is strikingly differ-

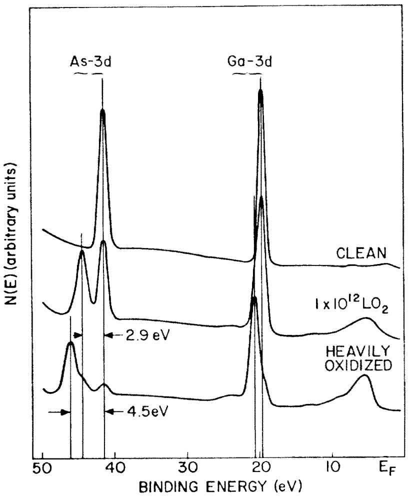

FIG. 3. Photoemission spectra ($h\nu = 100$ eV) of clean GaAs (110), after exposure to 10^{12} L of O_2 in the ground state and 10^6 L of O_2 excited by an ion gauge. The latter curve shows the effect of going beyond the chemisorption stage and the onset of bulk oxide formation.

ent from that of GaAs (110). Firstly, both the Sb 4*d* and the Ga 3*d* peaks are simultaneously shifted towards higher binding energy upon oxidation (with shifts of 2.6 and 1.1 eV, respectively). Secondly, the amplitudes of the shifted peaks grow steadily with increasing oxygen exposure (i.e., no saturation occurs). In the case of GaSb (110), the bonds between the surface atoms and the bulk are broken by adsorption of (unactivated) molecular oxygen, and the oxides form immediately on the surface. Introduction of excited oxygen from the ion gauge increases the rate of oxygen uptake but does not change the nature of the oxidation. Thus, it is clear that sorption on each surface of each semiconductor should be carefully studied and that the oxidation and effect of excited oxygen may differ greatly.

By making use of excited oxygen provided by the ionization gauge, we have carried out further oxidation experiments on the GaAs (110) surface trying to follow the different steps leading to bulk oxides by the photoemission technique. A cleaved (110) surface was first exposed to 10^{12} L, giving the results shown in the upper two curves of Fig. 3 with a 2.9-eV shift for the As 3*d* peak and no shift for the Ga 3*d* peak. The surface was then exposed to activated oxygen, produced by the ion gauge at 5×10^{-4} Torr of O_2 for 1000 sec. The resultant spectra (Fig. 3) show a second shifted As peak, $\Delta E = 4.5$ eV (attributed to As_2O_5), and a shifted Ga 3*d* peak (attributed to Ga_2O_3) in addition to the 2.9 eV-shifted As peak.[15]

In summary, the oxidation properties of the GaAs (110) surface can be described within the following model. The adsorption of molecular oxygen in the ground state results in oxygen (atomic or molecular) bonded to the As atoms as evidenced by a chemically shifted ($\Delta E = 2.9$ eV) As 3*d* peak and no shift for the Ga 3*d*. Saturation coverage is approached at about 10^{12} L O_2. Adsorption of oxygen excited by the ion gauge breaks the bonds between the surface atoms and the bulk, and true oxides (probably As_2O_5 and Ga_2O_3) start forming, as deduced from a second shifted As 3*d* peak ($\Delta E = 4.5$ eV) and a 1.0-eV-shifted Ga 3*d* peak. Furthermore, we have found that the oxidation of GaAs (110) and GaSb (110) surfaces proceed quite differently. Even when GaSb (110) is exposed only to unactivated oxygen, the second stage in the oxidation described for GaAs (i.e., bulk oxide formation) is observed but at a lower rate than for activated oxygen.

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[15] We have also exposed a freshly cleaved surface to activated oxygen from a much more intense discharge plasma and followed the oxidation process further. The As 3*d* peak attributed to As_2O_5 diminishes (As_2O_5 is volatile), whereas the 1.0-eV–shifted Ga 3*d* (attributed to Ga_2O_3) persists with unchanged strength. A further interesting observation is the energy position of the two remaining As 3*d* peaks, giving evidence for small amounts of elemental As and As_2O_3; P. Pianetta, I. Lindau, and W. E. Spicer, unpublished.