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Auger-electron spectroscopy, electron-energy-loss spectroscopy, and x-ray photoemission spectroscopy studies of oxygen adsorption on the InP(111)-(1×1) surface

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Auger-electron spectroscopy, electron-energy-loss spectroscopy, and x-ray photoemission spectroscopy measurements have been used to study oxygen adsorption on InP(111)-(1×1) surfaces and the initial stage of oxidation. It has been observed that oxygen is adsorbed on both surface In and P atoms on InP(111)-(1×1) surfaces at an oxygen exposure of 10^4 L O_2. (Here 1 L$\equiv10^{-6}$ Torr sec.) The mechanism of adsorption and oxidation is briefly discussed.

I. INTRODUCTION

InP is one of the most important semiconductor materials for the manufacture of photoelectronic and microwave devices. Unlike arsenic oxide, there is no instability problem with the phosphorus oxides, making the use of InP as a substrate material for metal-oxide-semiconductor structures even more attractive.[1] Beserman *et al.*[2] studied the effect of impurity on oxidation recently. However, the physics of the initial stages of the oxidation of InP is still controversial.[3-6] For a clean cleaved InP(110) surface, studies on the preferential chemisorption on only surface P (Refs. 3 and 4) have been published: Nedoluna[5] found different mechanisms under low and high exposures, while Goletti *et al.*[6] concluded that P oxide is formed earlier than In oxide. But our understanding of polar surfaces such as InP(111) and InP(100) which carry the preferential orientations for device-technology applications is still radimentary. We therefore utilize Auger-electron spectroscopy (AES), electron-energy-loss spectroscopy (ELS), and x-ray photoemission spectroscopy (XPS) to study the initial oxygen adsorption and oxidation of clean InP(111)-(1×1) surfaces.

II. EXPERIMENT

The experiments were performed on a VG ESCALAB-5 electron spectrometer facilitated with low-energy electron diffraction (LEED), AES, and XPS. The base pressure of this system is better than 5×10^{-9} Pa; the pressure is better than 2×10^{-8} Pa during the measurements. The sample was an n-type InP(111) single-crystal wafer with a carrier concentration of 6×10^{17} cm^{-3}, mechanicochemically polished and cleaned by standard procedures. A sharp InP(111)-(1×1) LEED pattern could be observed after argon-ion bombarding and annealing at 350 °C (IBA method). The cleanliness of the surface was checked by AES; no trace of O, C, or other impurities could be detected with AES. High-purity (99.99%) oxygen gas was introduced into the chamber by variable leak valves. The ion gauge was switched off to prevent the dissociation of oxygen molecules and to ensure that the surface was exposed to molecular oxygen ambient during oxygen exposure. Because the bonding in InP is weak, AES cannot distinguish between elemental In and In bonded in InP through the chemical shift,[7] and so we try to study the oxygen adsorption on InP(111)-(1×1) surfaces by the three techniques ELS, AES, and XPS. ELS data were taken with a primary-electron-beam current of 1–2 μA and 300-eV electron energy. All AES spectra were taken with a primary-electron-beam current of 5 μA at 3 keV. Great care was taken to minimize electron-beam effects. Electron-beam effects are minimized in AES and ELS due to low electron-beam current; no appreciable change can be detected in comparing the first AES and ELS spectra with subsequent ones. XPS spectra were taken using a Mg $K\alpha$ source ($h\nu=1253.6$ eV) with 50 eV pass energy of the hemispherical analyzer. The binding energy of XPS core level was calibrated with respect to E_F of the Ni 3d valence band.

III. RESULTS AND DISCUSSIONS

Because there are In islands on the In-rich InP(111)-(1×1) clean surface prepared by the IBA method, we first present the data of the oxygen adsorption on clean In metal surfaces in Sec. III A in order to distinguish the effect of the absorption on a clean ordered InP surfaces from that on In islands.

A. O_2/In metal surface

1. ELS

ELS data for the clean In metal surface versus the oxygen exposure are shown in Fig. 1. There are strong surface- and bulk-plasmon peaks, S_{In} and B_{In}, and double peaks associated with the In 4d core level on the curve of the clean In surface but no appreciable interband-transition peak can be detected. S_{In} and B_{In} peaks begin to decrease from very low oxygen exposure of 1 L O_2. [1 langmuir (L)$\equiv10^{-6}$ Torr sec.] Up to 10^3 L their relative intensities (with respect to the elastic peak) drop rapidly to near 0.2 from near 2.0 for the clean surface. In addition, the peak position associated with the In 4d core level rises to near 19.3 eV from near 18.2 eV for the clean surface, the double peaks associated with In $3d_{5/2,3/2}$ become a broad peak due to the broadening effect, and interband-transition peaks appear near 5 eV. Comparing it with the ELS spectrum of standard sample In_2O_3, we recognize the formation of a thick oxide layer on the In surface. In the range of exposure 10^4-10^6 L, the peak shape of ELS is nearly unchanged and the peaks S_{In} and B_{In} become stable.

2. *AES*

AES data for clean In metal versus oxygen exposure are shown in Fig. 2. For In *MNN* we define the height ratio R_1 ($\equiv I_{BC}/I_{CD}$) of between the low-energy peak *BC* and the high-energy peak *CD* and the height ratio R_2 ($\equiv I_{BC}/I_{AB}$) between the peak *BC* and the main peak *AB*. From 10^2 L, ratios R_1 and R_2 begin to decrease. Up to 10^3 L, the ratio R_1 drops to 0.77 (< 1) from 1.1 for the clean In surface and the ratio R_2 also decreases rapidly to 0.15 from 0.52 for the clean In surface. By comparison with the R_1 (< 1) of the standard sample In_2O_3, we showed the formation of a thick oxide layer on the clean In surface.

B. O_2/InP

1. *AES*

Characteristic Auger spectra In *MNN*, P *LVV*, and O *KLL* of clean and oxygen-covered InP(111)-(1×1) surfaces are shown in Fig. 3. Up to 10^4 L, for the P *LVV*

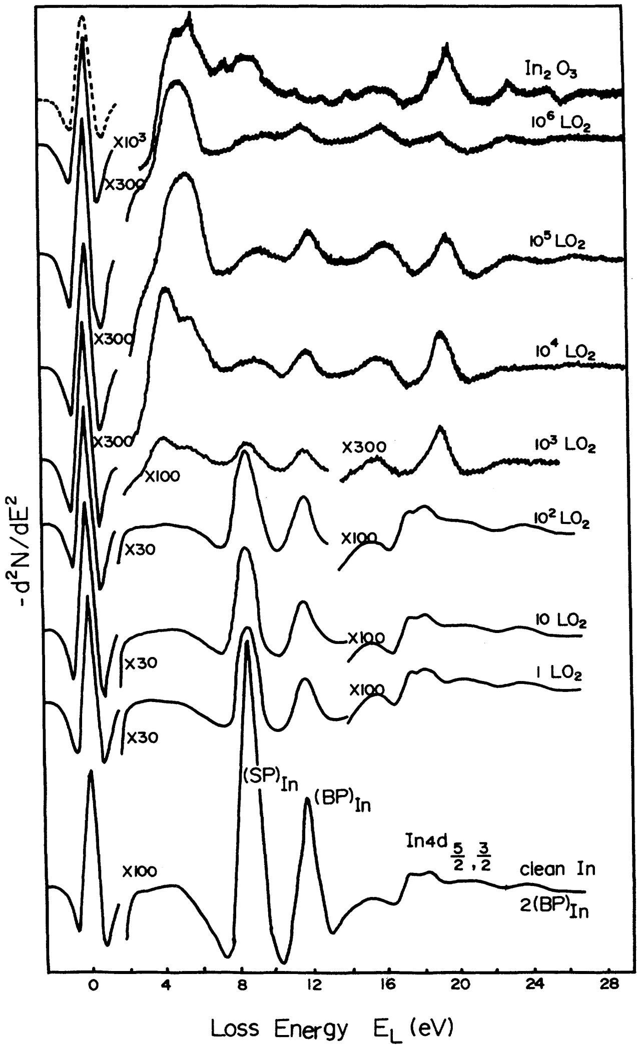

FIG. 1. ELS spectra of clean and oxygen-covered In metal foil surfaces.

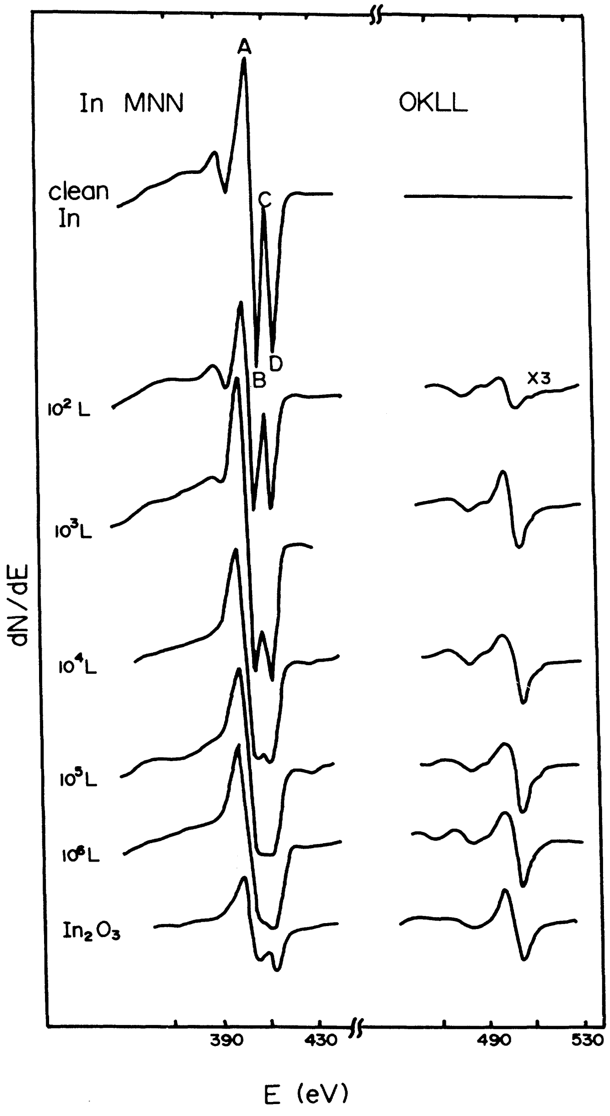

FIG. 2. AES spectra of clean and oxygen-covered In metal foil surfaces.

peak, with respect to the clean surface, the height ratio between the negative half-peak to positive half-peak decreases, and a small *G* peak appears at the low-energy end of the In *LMM* peak. It is shown that oxygen begins to adsorb on both surface In atoms and surface P atoms on the ordered InP surface simultaneously. At exposures up to 10^5 L, a small *H* peak appears at the high-energy end of the In *LMM* peak, and the height ratio R_1 decreases to less than 0.9 from larger than 1, and the height ratio R_2 decreases to 0.34 from 0.44 showing the beginning of a transition from the oxygen adsorption state to the In oxidation state on the ordered InP surface. We

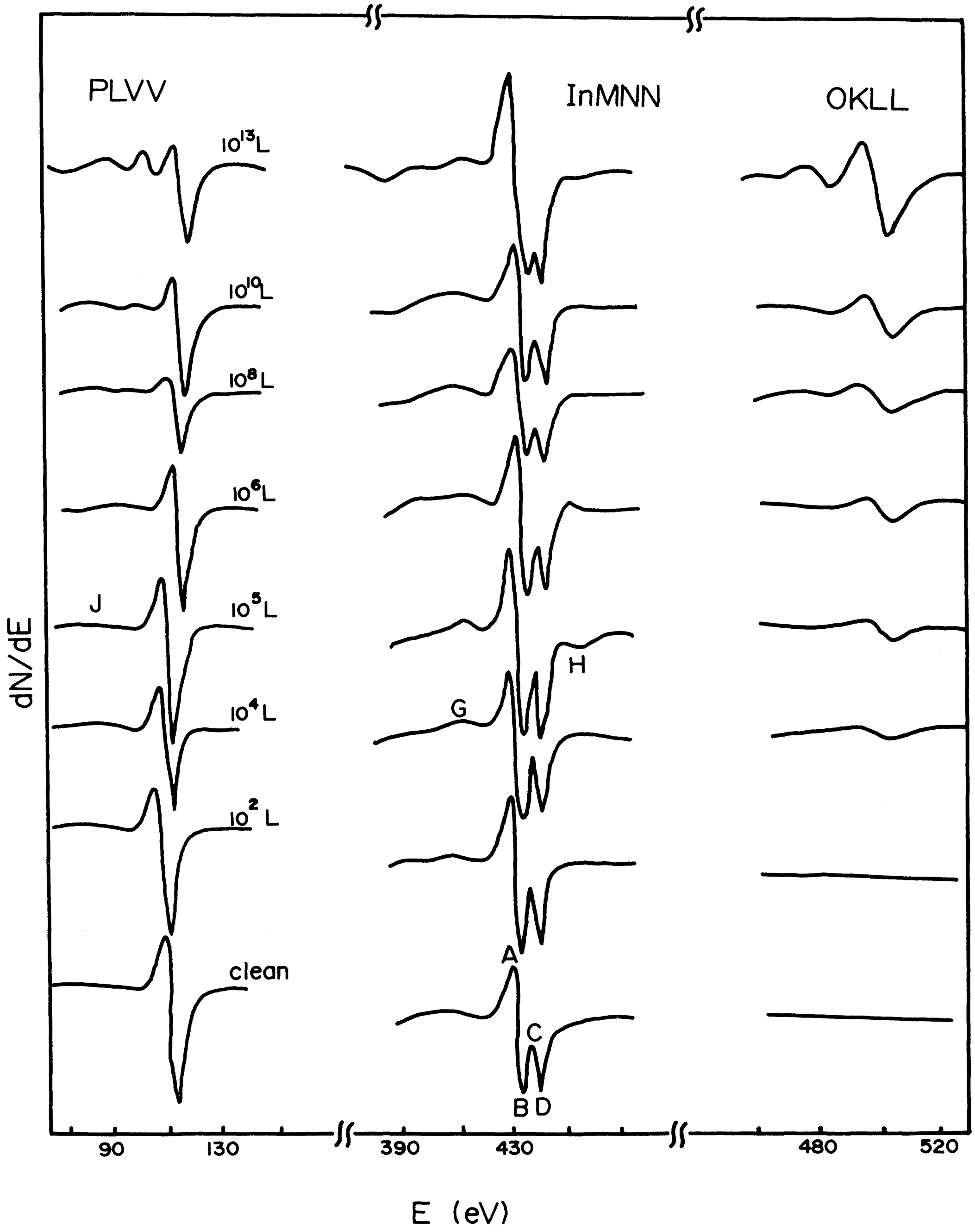

FIG. 3. In *MNN*, P *LVV*, and O *KLL* Auger spectra of clean and oxygen-covered InP(111)-(1×1) surfaces.

note that the rapid decrease of R_1 and R_2 for In metal is earlier than that of the ordered InP surface by two orders of magnitude in exposure. R_1 and R_2 decrease continuously in the range of 10^6 to 10^{13} L. And then R_1 and R_2 reach 0.75 and 0.13, respectively, at 10^{13} L. The shape of the In *MNN* peak at 10^8 L has some characteristics of In oxide. There is a small shoulder *J* on the lower-energy end of the P *LVV* peak at 10^5 L. Then up to 10^8 L two small characteristic peaks of P oxide can be detected at the low-energy end of the P *LVV* peak, which is similar to results of Oliver.[7] According to these results we suggest that In and P oxides form on InP(111)-(1×1) surfaces simultaneously. The P oxide and In oxide increase rapidly at about 10^8 L.

We note that the oxygen adsorption process can divide into three stages. (i) First, at 10^4 L the oxygen starts to adsorb on the ordered InP surface. (ii) Second, there is a slow increase from 10^5 to 10^8 L, which corresponds to a transitional stage from the adsorption process to the oxidation process. (iii) Above 10^9 L there is a rapid increase, which corresponds to the oxidation process. However, no evidence of oxygen saturation adsorption can be seen. It seems that the oxides appear to form at the very initial stages so that chemisorption of a full monolayer appears not to exist, which is very similar to the cleaved InP(110) surface.[4]

2. *XPS*

The XPS spectra of the P 2*p* core level of the clean and covered InP(111)-(1×1) surface are shown in Fig. 4. The changing of the shapes of In 3*d* and P 2*p* is not detected

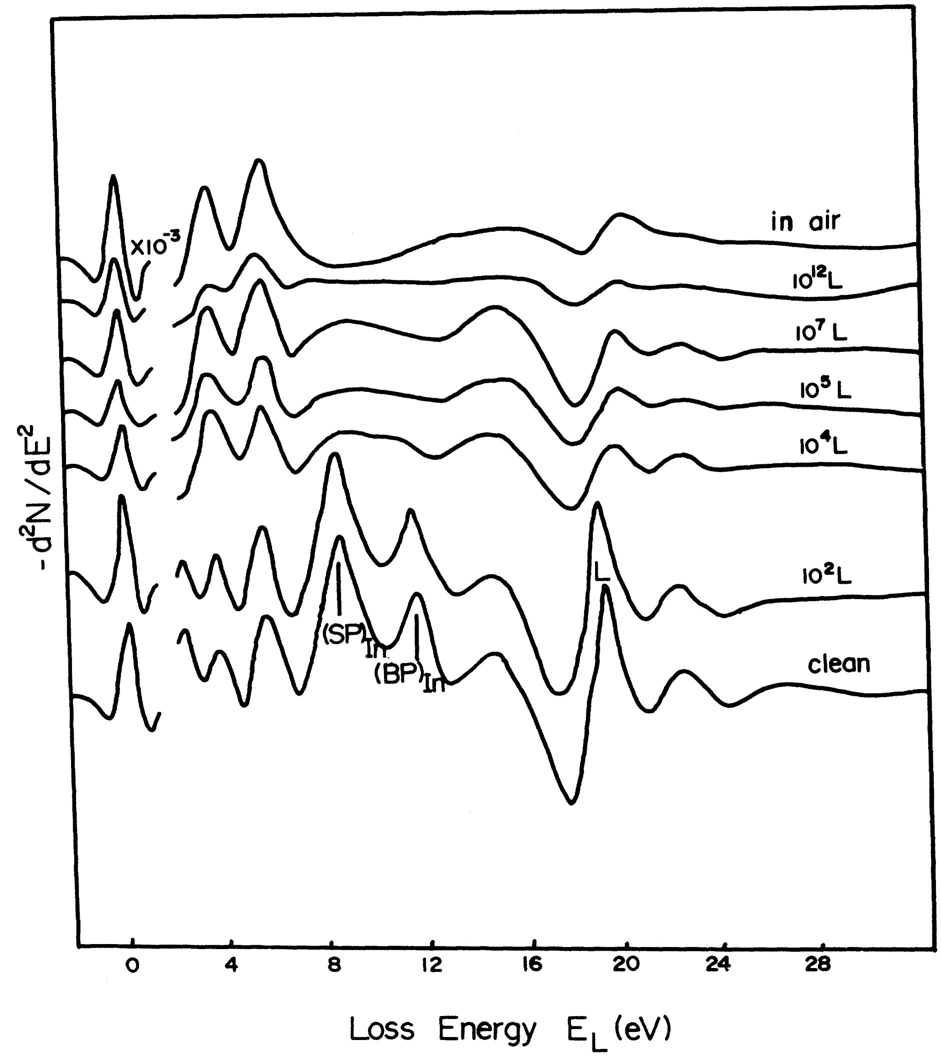

FIG. 4. P 2*p* core-level spectra of clean and oxygen-covered InP(111)-(1×1) surfaces.

until 10^7 L due to the lower sensitivity of XPS relative to AES. Up to a high exposure of 10^8 L, a 4.4-eV P 2*p* chemical shift indicates P oxide formation. At the same exposure, a slight broadening of In 3*d* can be observed and the FWHM (full width at half maximum) of In 3*d* rises to 1.88 eV with respect to the 1.85 eV of the clean surface. The XPS results also show that the In oxide and P oxide appear simultaneously at 10^8 L. And the FWHM of In 3*d* increases to 1.94 eV at 10^{10} L and this approach continues up to 10^{13} L. The FWHM of In 3*d* increases to 2.04 eV when the photoelectron emission angle decreases to 40°; the chemical shift is 0.25 eV with respect to the clean surface. The relative content of P oxide, with respect to surface P atoms, increases from 6% at 10^{10} L to 20% at 10^{13}. There, results show that there is a rapid growth of In oxide and P oxide above 10^{10} L.

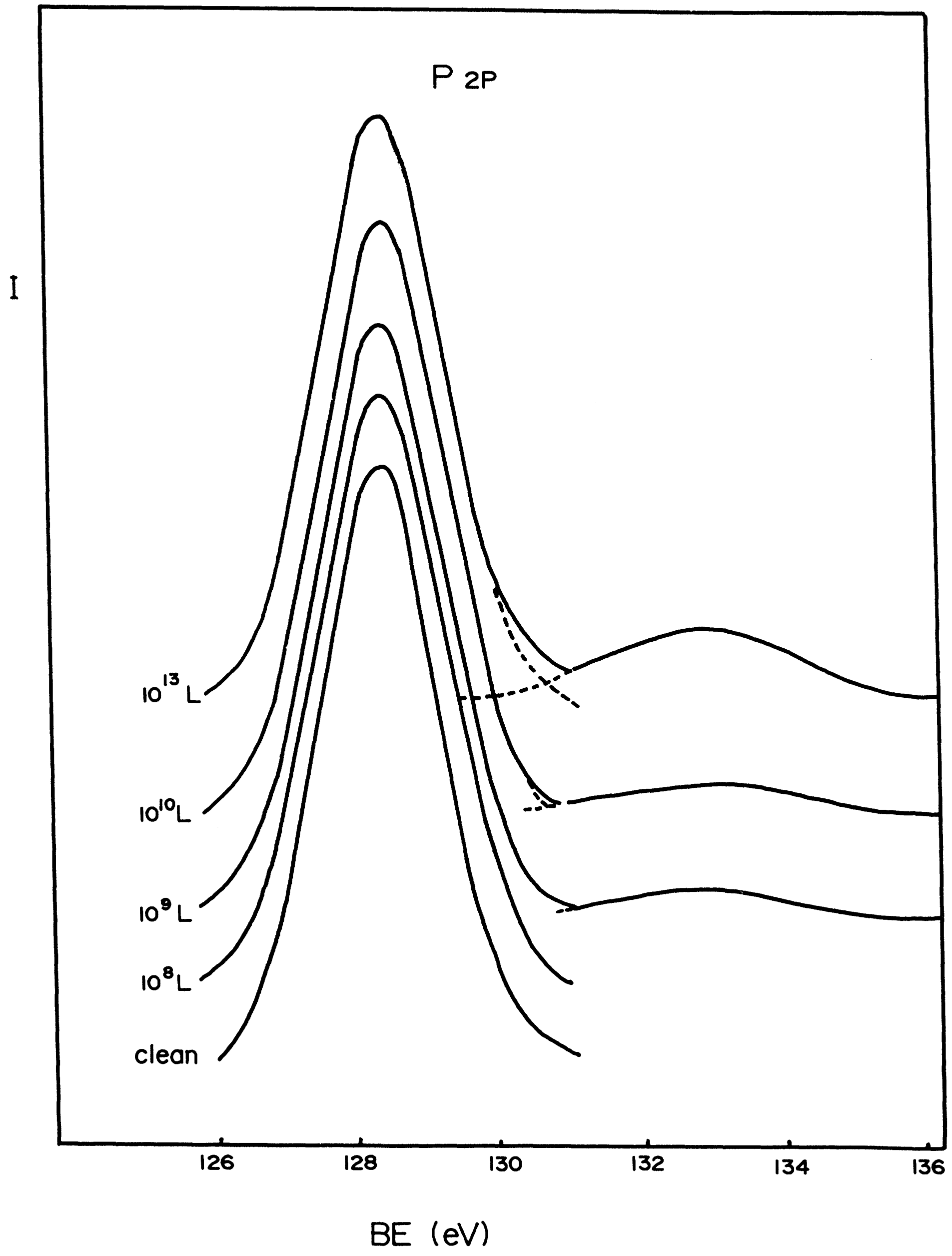

FIG. 5. ELS spectra of clean and oxygen-covered InP(111)-(1×1) surfaces.

3. *ELS*

ELS data shown in Fig. 5 also support the above AES and XPS results. This ELS spectrum of the clean surface is similar to that of Tu and Schlier.[8] Comparing it with the spectrum of the clean In metal surface, there are two strong peaks of S_{In} and B_{In} showing the In-rich and clean surface existence of In islands on the clean surface prepared by the IBA method. The area ratio R_A of In islands with respect to the InP surface is about 0.1 according to the relative ratio of the B_{In} peak between the InP surface and metal clean surface. Both the S_{In} and B_{In} peaks begin to decrease at a low exposure of 10^2 L and the rate of decrease of the S_{In} peak is faster than that of the B_{In} peak, showing that the oxygen adsorbs on In islands first. This adsorption process is nearly completed at 10^3 L. The loss peak L is associated with the In $4d$ core level excited to an unoccupied surface state near the conduction-band bottom. This L peak at 19.4 eV with a FWHM of 0.9 eV on the clean InP surface shifts to 19.9 eV with a FWHM of 1.3 eV at 10^4 L, showing oxygen adsorption on surface In atoms on the ordered InP surface. The L peak moves to 20.1 eV with a FWHM of 1.8 eV at 10^5 L, which is near 20.4 eV with a FWHM of 1.9 eV for native oxide on the InP surface in air, showing the formation of In oxide. These results are in good agreement with that of AES.

Because oxygen adsorption on the In metal surfaces occurs earlier by two orders of magnitudes in exposure than that for the ordered InP surfaces and $R_A < 1$ we can conclude that the adsorption on In metal islands has a rather small effect on the adsorption process of the ordered InP(111)-(1×1) surface, i.e., the data of Figs. 3–5 primarily show the adsorption process on the ordered InP(111)-(1×1) surface.

IV. DISCUSSION

According to the above AES, ELS, and XPS results and their comparison with data of the In surface, the oxygen adsorption process on InP(111)-(1×1) surfaces prepared by the IBA method can be divided into three steps: (i) oxygen adsorption on In islands of the clean InP surface for exposures ranging from 10^2 to 10^3 L; (ii) adsorption on both the In surface and P atoms of the ordered InP surface at an intermediate exposure of 10^4 L; (iii) formation of In oxide and P oxide at a high exposure of 10^8 L and continuous growth of both oxides until a very high exposure of 10^{13} L. This result is different from that of the cleaved InP(110) surface by Spicer and coworkers[4] which may be due to differences in surface preparation with the IBA method.

Because there are more defects on InP(111)-(1×1) surfaces prepared by the IBA method, we assume that first the oxygen is adsorbed on the weak bond, such as the steps and defects on the ordered InP clean surface, and then adsorbed on the order InP(111); as Mark *et al.*[9] pointed out, sufficient energy is given up in oxygen adsorption to break surface InP bonds and to produce the defects which might act as active sites, so that In oxide and P oxide can appear at high oxygen exposures.

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