

InP(110) oxidation with O₂, NO, and N₂O at 20 K: Temperature and photon-energy dependencies

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Interfaces formed at 20 K by condensing O₂, NO, and N₂O on InP(110) reveal striking differences in reactivity when they are heated, illuminated with visible light, or irradiated with soft x rays [$h\nu=170$ eV, photon exposures of $(1-1000)\times 10^{14}$ cm⁻²]. Synchrotron-radiation photoemission studies show that O₂ and N₂O desorb from the surface without reacting when annealed above ~ 100 K but that oxidelike In and P bonding configurations are produced by NO reactions when heated to ~ 150 K. Flood-lamp illumination induces reaction for O₂/InP and NO/InP at 20 K but not for N₂O/InP ($h\nu=0.5-4.5$ eV, photon exposure $\sim 10^{19}$ cm⁻²). Irradiation with 170-eV photons yields surface oxides for all three oxygen-bearing condensates. Investigations of the reaction cross sections for these systems indicate that surface chemistry is mediated by the capture of photogenerated low-energy electrons. Electron-attachment processes that produce negative ions are less likely for N₂O than for NO or O₂.

Photon-induced oxidation of III-V semiconductor surfaces is scientifically challenging and technologically important. Many excellent studies of GaAs(110) oxidation have been conducted as a function of temperature,¹⁻³ oxidizing gas,^{2,4-6} and photon energy.⁷ The most recent work has focused on the dynamics of photon-induced reactions at temperatures where the reactant is condensed on the surface.^{6,8-10} These condensed-layer systems have exhibited temperature and photon-energy dependencies, and it has been shown that the experimental probe (photoemission) induces both reaction and desorption.^{8,9} In general, it has been concluded that substrate electronic excitations are responsible for photon-induced oxidation, but a consensus on the role of these excitations has yet to be reached.

In this paper, we report the first studies of the interactions of the condensed oxidizers O₂, NO, and N₂O on InP(110) at 20 K. These gases were chosen because they oxidize InP,^{1,11-13} they are sensitive to light exposure, and they exhibit different thresholds for photon- and electron-induced decomposition. Core-level and valence-band studies indicate that each is adsorbed molecularly on InP(110) at 20 K, but that striking differences are revealed upon heating above ~ 100 K or illuminating with visible light and soft x rays. In particular, condensed NO reacts with InP when annealed to 150 K but condensed O₂ and N₂O simply desorb. Illumination of the condensed-gas/InP(110) surface with a high-intensity flood lamp induces InP oxidation with O₂ and NO but not with N₂O (total exposure $\sim 10^{19}$ photons cm⁻²). Irradiation with 170-eV photons promotes reaction with all three gases, O₂, NO, and N₂O. The differences can be understood by considering the effect of temperature on the adsorbate-semiconductor system and the role of negative ions formed via capture of photogenerated electrons.

High-resolution photoemission experiments were conducted at the Wisconsin Synchrotron Radiation Center. Energy distribution curves (EDC's) were acquired with a

double-pass cylindrical mirror analyzer that, when combined with monochromator contributions, yielded an overall resolution of ~ 400 MeV for the P 2*p* core levels that will be the focus of this paper. Valence-band and In 4*d* core-level results supporting our conclusions will be reported elsewhere. Posts of InP (S doped, $N_D=2.7\times 10^{18}$ cm⁻³) were cleaved at pressures of $\sim 5\times 10^{-11}$ Torr to yield pristine (110) surfaces. Nearly identical chemical trends were measured for *p*-type InP. All of the results were obtained with samples for which the clean surface Fermi level E_F was less than 60 meV from the band edge at 300 K.

The gases O₂, NO, and N₂O were introduced into the experimental chamber through a calibrated leak valve. The gas line was flushed during and after bakeout because NO and N₂O decompose by reaction with the chamber walls.^{4,8} Inspection of the valence-band emission immediately after gas exposure gave no evidence for contaminants. Gas exposures (in langmuirs where 1 L=1×10⁻⁶ Torr sec) were measured with the ion gauge without correction for gauge sensitivity. Results acquired for dosing the sample with the gauge on and off were nearly identical, indicating a negligible effect on molecules condensed on the surface. The ion gauge was off except during gas dosing or sample heating, and the sample remained in the dark except during irradiation with synchrotron radiation or the flood lamp.

Figure 1(a) presents P 2*p* core-level results obtained after the exposure of InP(110) to 4-L NO, 2-L O₂, and 4-L N₂O at 20 K followed by warming above 100 K. The purpose was to determine whether adsorption and desorption were reversible in the absence of an electron source or photon probe, i.e., whether there would be thermal conversion from physisorbed to chemisorbed states. Gas exposures were chosen to condense approximately equal numbers of oxygen atoms on the surface. Each spectrum has been normalized to constant height to emphasize line-shape changes, and the bulk features have been aligned. EDC's obtained after N₂O and O₂ conden-

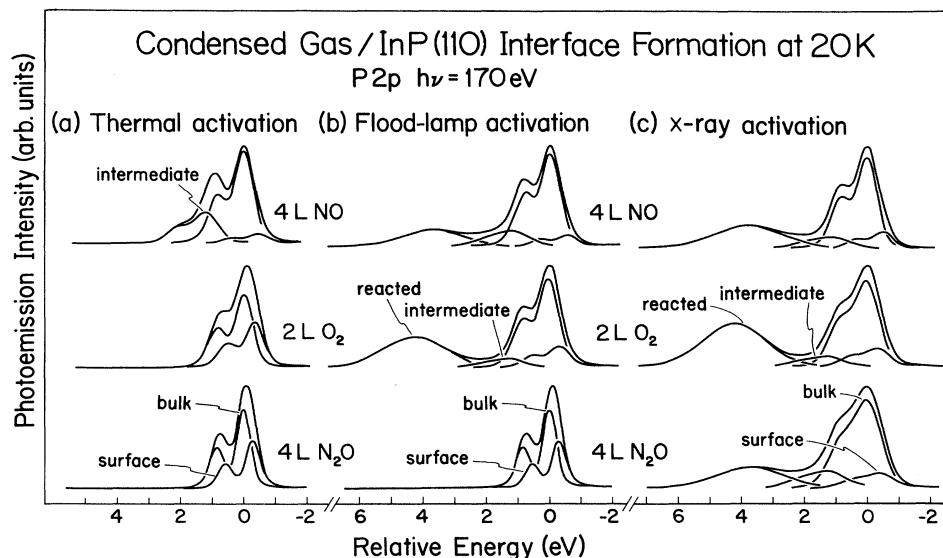


FIG. 1. (a) P $2p$ core-level EDC's for 4-L NO, 2-L O₂, and 4-L N₂O condensed on InP(110) in the dark at 20 K and then annealed to desorb the gas. The N₂O and O₂ spectra show no substrate disruption. In contrast, annealing NO-covered surfaces to 150 K results in the formation of bonding configurations characteristic of an intermediate oxide. (b) P $2p$ EDC's after illumination by a flood-lamp ($h\nu=0.5\text{--}4.4$ eV). Surfaces exposed to O₂ and N₂O were annealed above 100 K before data acquisition. The spectra for the NO-exposed surface were acquired with a minimum of photon irradiation to avoid x-ray-induced oxidation. No reaction was observed for N₂O, but two reaction-induced P peaks appeared for O₂ and NO. (c) P $2p$ EDC's after irradiation with soft x rays ($h\nu=170$ eV) showing reaction for all three molecules.

sation at 20 K and heating were indistinguishable from those of the clean surface, exhibiting only surface-shifted and bulk P peaks (although the Gaussian linewidths did increase 20–50 meV due to thermal broadening). This indicates that N₂O and O₂ desorb from the surface without inducing measurable oxidation or surface unrelaxation. (The spectral linewidths are broader for O₂/InP because of the monochromator resolution in that experiment.) In contrast, warming from 20 to 150 K for 4-L NO/InP(110) resulted in strong adatom-substrate interactions as a component formed ~ 1.2 eV from the bulk P feature and as emission from the surface-shifted peak decreased. This new feature corresponds to an intermediate P oxide, as reported by Hollinger *et al.*¹¹ in their high-resolution study of O₂/InP(110) reaction at 300 K.

In Fig. 2 we present schematic Lennard-Jones-type potential-energy curves for physisorption and chemisorption to the observed low-coverage interactions of O₂, NO, and N₂O with InP(110) as a function of temperature. Physisorption is represented by a van der Waals potential that has a minimum at E_p . Splitting the molecule into atoms far from the surface requires a dissociation energy E_d while atom-substrate interactions lower the energy of the system to E_c , the chemisorption energy. The activation energy for dissociative chemisorption E_a is the energy difference between E_p and the intersection of the chemisorption and physisorption potential-energy curves, as sketched. For NO, $E_a < E_p$, and the incoming molecule can be trapped in a physisorption well without reacting with the substrate.¹⁴ Heating the NO/InP(110) system excites vibrational modes of the molecule and, since

the barrier for reaction is smaller than for molecular desorption, NO-InP chemical interactions are observed, as in Fig. 1(a).

The thermally induced reactions for NO/InP(110) contrast with what is seen for O₂ and N₂O on InP(110).¹⁵ Since O₂ and N₂O desorb upon heating above ~ 100 K,

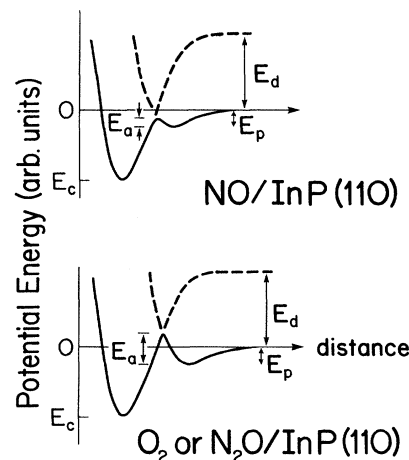


FIG. 2. Schematic potential-energy functions for dissociative chemisorption that describe the temperature-dependent results of Fig. 1(a). The curves for NO/InP(110) indicate that the physisorbed molecule can overcome the chemisorption barrier upon vibrational excitation (annealing). For O₂ and N₂O, physisorption and chemisorption potentials intersect above zero, favoring desorption upon heating.

we conclude that the intersection of their potential-energy curves for physisorption and chemisorption is such that $E_a > E_p$, as drawn in Fig. 2. The observed behavior for O₂/InP(110) was not surprising, based on the results of Bertness *et al.*⁴ for O₂/GaAs(110). They found that E_a was ~ 0.45 eV and E_p was ~ 0.15 eV for O₂/GaAs(110) at 300 K, in reasonable agreement with the barrier of ~ 0.3 eV reported by Mönch.¹ For N₂O/InP(110), however, the results of Fig. 1(a) demonstrate that there was desorption with little reaction, and this is opposite the conclusion of Bertness *et al.*⁴ for N₂O/GaAs(110). Indeed, they reported values of $E_a \sim 0.15$ eV and $E_p \sim 0.25$ eV, indicating that chemisorption should be favored over desorption.⁴ For N₂O, the apparent contradiction probably reflects the fact that the experiments were done at different temperatures. At low temperature, physisorption is an important step, as is the case for our results. At high temperature, it is not necessarily the precursor state of chemisorption, and direct impact of N₂O with the surface may yield the chemisorbed state directly. This reaction path was not considered by Ref. 4. We also note that studies of N₂O-GaAs(110) interactions at 20 K have shown that $E_a > E_p$ and the N₂O condensed at low temperature does not react with GaAs(110) to any appreciable extent when warmed to 300 K.¹⁶ Thus, thermally activated interactions of O₂ and N₂O with GaAs(110) and InP(110) are analogous and they can be understood from Fig. 2.

To further examine the stability of O₂, NO, and N₂O condensates on InP(110), we illuminated these systems with a high-intensity flood lamp. The bottom EDC of Fig. 1(b) shows the result of illumination of 4 L N₂O/InP(110) for 15 min (exposure $\sim 10^{19}$ photons cm⁻², spectral range 0.5–4.5 eV) followed by warming to 140 K to remove any unreacted physisorbed molecules. Since no significant line-shape changes relative to the clean surface were observed, we conclude that low-energy photons induced minimal reaction between N₂O and InP(110). In contrast, illumination of 2 L O₂/InP(110) followed by heating to 100 K produced considerable surface oxidation, as indicated by the features shifted ~ 1.2 and ~ 4 eV from the bulk peak of Fig. 1. Analogous features have been observed for O₂/InP(110) at 300 K, although at 10^6 – 10^{12} higher O₂ exposures.^{3,11} Hence, low-energy photon irradiation can effectively promote oxide growth at 20 K for O₂ condensed on InP(110). For 4-L NO/InP(110), flood-lamp illumination induced surface modifications, as is evident by the growth of structure ~ 1.2 and ~ 3.5 eV from the bulk peak, as shown in Fig. 1. Note that this EDC was acquired immediately after flood-lamp illumination at 20 K because heating by itself alters the surface chemistry [Fig. 1(a)]. Moreover, the x-ray exposure needed to acquire the data was much less than that used to induce the reaction depicted in Fig. 1(c). We also note that annealing the NO-covered InP(110) surface above 150 K produced the ~ 3.5 -eV peak (not shown). Warming to 300 K or exposure to additional NO and flood-lamp illumination shifted the 3.5-eV peak toward 4 eV. Hence, flood-lamp illumination produced similar oxides for NO/InP and

O₂/InP but there was almost no effect for N₂O/InP.

In Fig. 1(c) we show the effects of soft-x-ray irradiation of these condensed layers on InP(110) at 20 K. Surface oxides are produced in each case, and the spectra for soft-x-ray irradiation of O₂ and NO are similar to those for flood-lamp illumination [Fig. 1(b)]. Exposure of 4-L N₂O/InP(110) to 170-eV photons results in two new P components at ~ 1.2 and ~ 3.5 eV. Comparison of the photon-induced reactions for N₂O/InP to those for O₂ and NO illustrates the similarity between the oxides formed at 20 K when the amount of condensate is small. Differences can be attributed to differences in the total number of O atoms available for reaction, the kinetics of molecular decomposition and reaction for each molecule, and photon-stimulated desorption from the surface. The results of Figs. 1(b) and 1(c) are particularly intriguing because they show that soft-x-ray irradiation led to surface oxidation in all three cases but that low-energy irradiation produced a reacted surface only for NO and O₂.

In general, photoinduced oxidation reflects direct adsorbate excitation by the photon and indirect adsorbate excitation via capture of electrons produced by photon absorption in the substrate. The relative roles of these processes can depend on photon energy.⁷ For the systems under investigation here, we can show that direct excitation plays a minor role. In particular, in the flood-lamp illumination experiments only that portion of the blackbody distribution that was transmitted through the glass viewport was available for excitation (0.5–4.5 eV). These low-energy photons cannot dissociate O₂ ($E_d = 5.1$ eV) or NO ($E_d = 6.5$ eV) to produce neutral, ground-state atoms.¹⁷ For N₂O, the lowest-energy mode for optical dissociation (1.67 eV) is spin forbidden, but photolysis into ground-state N₂ and excited O is possible. However, illumination with $\sim 10^{19}$ photons cm⁻² would cause photolysis of less than 0.1% of the N₂O molecules,¹⁸ and such a yield is below our detection limit. Thus, the reactions summarized in Fig. 1(b) for O₂, NO, and N₂O, are not related to direct photon absorption by the molecule. Indeed, the effect of flood-lamp irradiation is smallest for the molecule for which direct absorption might play a role, namely N₂O.

Processes that involve direct photoexcitation of overlying molecules and/or substrate atoms in contact with the molecules can also be excluded as major reaction channels by comparing photoionization cross sections to the effective cross sections for the photoinduced reactions. From the photoemission results, it is possible to determine a lower bound for the reaction cross section by measuring the rate of conversion of the surface-shifted P 2*p* core-level peak as a function of photon exposure. If we assume that reaction for each molecule proceeds by a first-order process and that only the topmost layer of InP atoms is affected initially,¹⁹ then kinetic theory predicts that the relative emission of the surface-shifted component varies with photon exposure as $\ln[I(E)/I(0)] = -\sigma E$, where $I(0)$ is the intensity of the surface component after condensation, σ is the cross section, and the units of exposure E are photons cm⁻². Our analysis of O₂, NO, and N₂O interactions with InP(110)

at 20 K reveals cross sections of $\sim 6 \times 10^{-15}$, 1×10^{-15} , and 4×10^{-16} cm²/photon, respectively, for 170-eV photons.²⁰ These reaction cross sections are about two orders of magnitude greater than the photoionization cross sections for either the molecule or the substrate at 170 eV.²¹ Thus, surface reactions proceed more rapidly than expected for direct photon-absorption processes.

Indirect photon-induced oxidation mechanisms can depend on positive-ion formation, negative-ion formation,^{1,3,5} and electron-hole recombination events (non-thermal phonons).^{2,4} Positive-ion formation can be discounted here because the energies of formation for the positive ions are greater than the dissociation energies of the neutral molecules.²² Negative-ion formation can be examined in terms of the potential-energy curves of Fig. 3, where we show results for gas-phase NO, O₂, N₂O (solid lines), and for the lowest negative-ion states (dashed lines).^{17,22-24} Figure 3 focuses on the lowest-energy excitation processes since the experimental results show that low-energy photons can induce reaction, at least for O₂ and NO. We assume that the negative ion is more reactive than the neutral molecule and that reaction with the substrate proceeds once the ion is formed. Dissociation energies are given by the difference between the energy at the equilibrium bond distance and at infinite interatomic spacing. These dissociation energies are 6.5 eV for NO

and 5.1 eV for O₂.²² The potential for N₂O is plotted as a function of the N-O separation, and dissociation into ground-state N₂ and O requires ~ 1.7 eV.²⁴ Again, the experimental results show that the dissociation energy of the molecule is not the critical parameter for predicting photoinduced InP(110) surface oxidation at low temperature. Indeed, they stand in contrast to the expectation that photoinduced surface oxidation should increase for molecules with low dissociation energies.¹⁻⁵

The potential-energy curves for N₂O–N₂O[−] are quite different from those for NO–NO and O₂–O₂[−], as can be seen from Fig. 3. (The vibrational levels of the neutral molecule and the ion that determine the allowed Franck-Condon transitions are not shown.) For gas-phase N₂O, an electron with ~ 2.2 eV is required to excite the molecule from the neutral ground state to an unstable N₂O[−] ion state that can decompose into N₂ and reactive O[−]. In contrast, electron capture to form the corresponding NO[−] or O₂[−] ions requires less than 0.2 eV. Comparison of these potential-energy diagrams for gas-phase molecules to the experimental results of Fig. 1 strongly suggests that negative-ion formation controls photon-induced oxidation.

In order to understand the details of electron capture, it is necessary to know the distribution of carriers in the conduction band of InP and the molecular levels of the adsorbate. However, when the molecule approaches a surface, the molecular energy levels are shifted by image potentials that lower (raise) the electron affinity (ionization energy),²⁵ and when charge transfer from a conduction-band state to the molecule occurs, the molecule-substrate potential is replaced by an ion-substrate potential.²⁶ For ion formation to occur, the energy of a conduction-band electron must align with the molecular (ion) level. Electrons in the conduction band exist because of thermal excitation or photon absorption. The former produces carriers near the conduction-band minimum while the latter provides a large number of secondary electrons with a range of energies. Inspection of Fig. 3 shows that alignment of the electron affinity levels of NO, O₂, and N₂O (or equivalently, the negative-ion curves) to a given conduction-band level of InP(110) would require that the electron affinity of N₂O be reduced by ~ 2 eV more than that of either O₂ or NO when the molecule approaches the surface. This is evident from the fact that the electron affinities of the molecules are -2.2 eV for N₂O, 0.1 eV for NO, and 0.45 eV for O₂. From the experimental results, we see that the reaction cross sections for N₂O, NO, and O₂ on InP(110) correlate with these electron affinities, and this probably explains the very different behavior of these gases on InP(110). The experimental results therefore support the idea that negative-ion formation is a limiting factor in photoinduced oxidation. Indeed, the importance of electron-attachment processes has been discussed extensively,^{7,20,26-28} although incorporation of these processes in a quantitative model of photon-induced surface reactions remains to be done.

In summary, photoemission studies of low-temperature oxidation of InP(110) with O₂, NO, and N₂O reveal

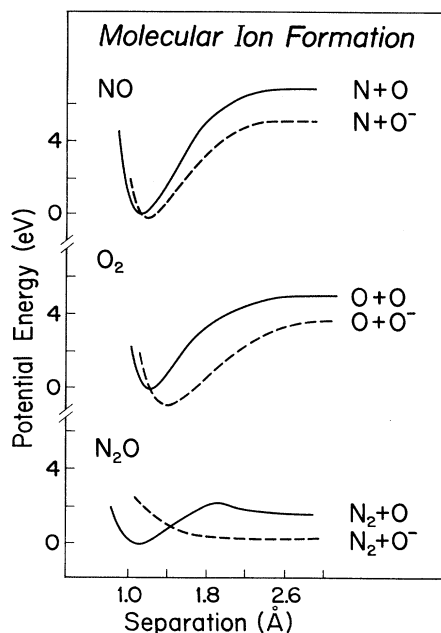


FIG. 3. Gas-phase potential-energy curves for NO, O₂, N₂O, and their ions. The zero-energy point is defined as the ground-state molecule at equilibrium separation. The N₂O potential plotted as a function of N-O separation exhibits no stable minima for the ion. Dissociation of N₂O requires the capture of a ~ 2.2 -eV electron. NO and O₂ form metastable reactive ions upon capture of ~ 0.2 -eV electrons. Differences in reactivity for the three gases are attributed to the relative ease of reactive-ion formation.

strong temperature and photon-energy dependencies that can be understood by considering the competition between pathways for molecular decomposition and reaction. Photon-energy-dependent results indicate that the probability of negative-ion formation must be considered in low-temperature oxidation. Additional clarification of the role played by excited carriers in photoinduced oxidation should result from investigations conducted with monochromatic low-energy photons⁷ and low-energy electron beams, and such studies are underway.

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