Precursor molecular-oxygen state in the initial catalytic oxidation of the InP(110) surface modified by alkali metals

P. Soukiassian*
Department of Physics, Northern Illinois University, DeKalb, Illinois 60115
and Synchrotron Radiation Center, University of Wisconsin–Madison, Stoughton, Wisconsin 53589-3097†

M. H. Bakshi,‡ H. I. Starnberg, A. S. Bommannavar, and Z. Hurych
Department of Physics, Northern Illinois University, DeKalb, Illinois 60115
(Received 21 September 1987)

The kinetics and the mechanism of the oxidation of the InP(110) surface modified by a cesium monolayer have been studied by valence-band and core-level photoemission spectroscopy using synchrotron radiation. The presence of a Cs monolayer on the InP(110) surface leads to an exceptional enhancement of the oxidation rate by 13 orders of magnitude with formation of phosphates such as $InPO_4$. In strong contrast with cesiated transition-metal surfaces, we find a precursor state of molecular oxygen prior to the onset of InP(110) oxidation. At higher exposures, both molecular- and atomic-oxygen states coexist in a dynamic equilibrium.

Surfaces of III-V semiconductors are in general not very sensitive to oxygen adsorption and therefore not very easy to oxidize. Although among the III-V semiconductors most of the attention has been focused on gallium arsenide, indium phosphide has recently received considerable attention because of its expected greater usefulness in metal-insulator-semiconductor (MIS) devices.[1] *Molecular*-oxygen exposures between 10^{12} and 10^{13} L [1 langmuir (L) $=10^{-6}$ Torr sec] are generally required to form thin oxide layers on InP(110) (Refs. 2–4) while 10^5 L of *atomic* oxygen is sufficient to obtain the same result.[2,3] While the oxide consists mainly of phosphates, the existence of indium oxide such as In_2O_3 has also been reported.[2] A way to minimize the oxygen exposures necessary for the oxidation of semiconductors is the use of catalysts such as noble metals, transition metals, and rare-earth metals which have been found to be successful for silicon in various cases.[5] Recently, alkali metals have been shown to be efficient electronic promoters of silicon oxidation. At room temperature, cesium, sodium, and potassium enhance the silicon oxidation rate by several orders of magnitude (4–6) forming mainly oxide where the silicon is primarily bonded to three atoms of oxygen.[6,7] By flash annealing at moderate temperature a SiO_2-Si interface is formed.[6] Furthermore, the alkali-metal catalysts are desorbed and removed from the surface by this thermal treatment.[6,7] The three alkali metals were found to have basically the same effect on silicon oxidation by (i) weakening of the silicon back bonds, (ii) enhancing the oxygen sticking coefficient, and (iii) dissociating the oxygen molecule.[6] On III-V semiconductors, Cs is known to exhibit a significant catalytic activity in promoting oxidation of GaAs.[8] We have shown that a Cs monolayer enhances the oxidation rate of (110) face of indium phosphide by as much as 13 orders of magnitude, which is the largest promotion effect ever observed.[9] In this Brief Report we provide further insight into the mechanisms leading to this catalytic oxidation by reporting the existence of a molecular-oxygen precursor state, in strong contrast with cesiated transition-metal surfaces. From this molecular precursor state, oxygen dissociates into an atomic state thus initiating the oxidation of the InP(110) substrate.

The photoemission experiments were performed in an ultrahigh-vacuum chamber at a pressure of 4×10^{-11} Torr. The light emitted by the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin–Madison was dispersed by a Grasshopper Mark II monochromator. The experimental arrangements are described in more detail elsewhere.[5,6,9]

Figure 1 displays the P 2*p* core level after deposition of one cesium monolayer, followed by increasing exposures to molecular oxygen between 0.25 and 64 L. Below 1 L of oxygen, the P 2*p* core-level spectra do not exhibit any chemical shift, indicating that no oxidation is taking place in this range. Exposures ranging from 1 to 64 L of molecular oxygen leads to a new peak *B* shifted by 4 eV to higher binding energy compared with the original P 2*p* core level.[9] The intensity of this new peak *B* increases with further O_2 exposure. This indicates the growth of phosphates, mainly $InPO_4$.[1–4] Saturation occurs around 20 L.[9] No evidence for indium oxide formation was found in the In 4*d* core-level spectra,[9] but as the corresponding chemical shift is rather small, it is still possible that a small amount of In_2O_3 was formed as reported by Bertness *et al.*[2] for the O_2/InP(110) system. Without a Cs layer, a 10^{13}-L exposure to molecular oxygen is known to be necessary to obtain a comparable amount of $InPO_4$.[4] Therefore the Cs overlayer enhances the oxidation rate of indium phosphide by nearly 13 orders of magnitude, which is the largest oxidation enhancement ever observed for a semiconductor surface.

 ©1988 The American Physical Society

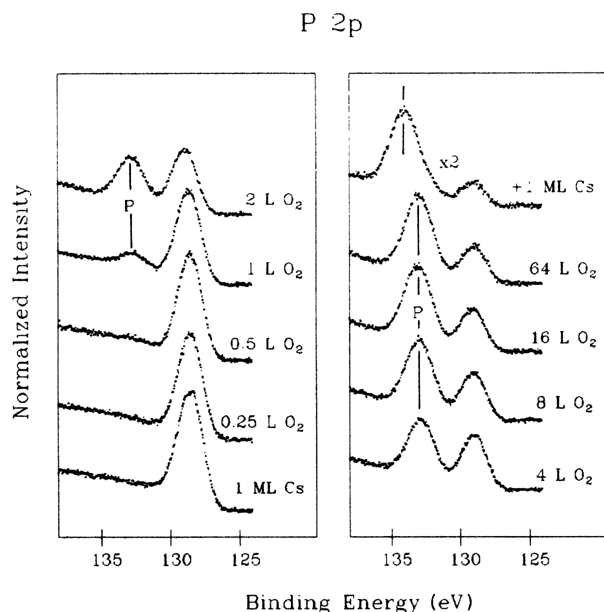

FIG. 1. Phosphorus $2p$ core-level spectra of O_2/1 ML Cs/$InPO_4$ for molecular-oxygen exposures between 0.25 and 64 L (Ref. 8) (ML stands for monolayers). The photon energy was 170 eV. Peak P indicates the chemical core-level shift.

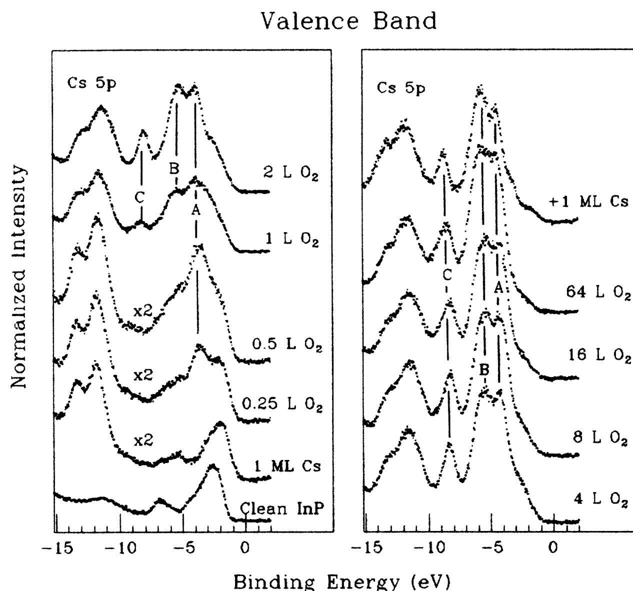

FIG. 2. Valence-band spectra of O_2/1 ML Cs/InP(110) for molecular-oxygen exposures between 0.25 and 64 L. The photon energy was 82 eV. The Fermi level of the cesiated InP(110) surface is chosen as reference for the binding energies.

Figure 2 shows the corresponding valence-band spectra for a cesium monolayer deposited on an InP(110) surface and subjected to increasing molecular oxygen exposures between 0.25 and 64 L. With the deposition of a monolayer of cesium a new electronic structure appears at 5.5 eV below the Fermi level. It is likely due to a Cs-induced interface state. A similar peak is also observed on the K/GaAs(110) and Cs/GaAs(110) interfaces.[10] We will discuss this point in detail elsewhere. At an oxygen exposure of 0.25 L, a new peak A corresponding to the oxygen $2p$ level appears at 4 eV binding energy. This peak is related to the existence of molecular oxygen.[11] The comparison of this result to the direct interaction of molecular oxygen with the (110) face of indium phosphide[3] shows that the cesium monolayer dramatically enhances the oxygen sticking coefficient. The intensity of peak A grows with increasing exposures up to 1 L. At this last exposure, two additional peaks, B and C, also related to O $2p$ levels, emerge at 6 and 8.5 eV below the Fermi level, respectively. The appearance of peaks B and C corresponds to the formation of atomic oxygen[3] and it also marks the onset of indium phosphide oxidation as seen from the P $2p$ core-level spectra (cf. Fig. 1). Peaks B and C are related to nonbonding and bonding O $2p$ states, respectively. Their binding energies agree with the valence-band measurements of excited oxygen adsorbed on InP(110) by Hollinger *et al.*,[3] but their relative intensities are somewhat different. Our results demonstrate that the dissociation of oxygen plays a crucial role in the catalytic oxidation of indium phosphide. Furthermore, the intensity of the O $2p$ levels increase with increasing molecular exposures. However, the relative intensities of peaks A and B remain about the same for oxygen exposures between 2 and 64 L. This indicates the coexistence of both molecular and atomic oxygen in a dynamic equilibrium. It is consistent with the rapid saturation of $InPO_4$ growth which is observed at oxygen exposures above 20 L.[9]

This equilibrium is disrupted in favor of atomic oxygen by the addition of another equivalent cesium overlayer on top of the 64 L O_2/Cs/InP(110) system, as can be deduced from the increased intensity of peak B relative to peak A (Fig. 2). It is evident from the corresponding P $2p$ spectra in Fig. 1 that the $InPO_4$ thickness also increases as does the chemical shift (4.5 instead of 4 eV), likely due to the formation of more stoichiometric phosphates. Interestingly, cesium does not give rise to a similar precursor state of molecular oxygen on transition-metal surfaces,[12] where oxygen is dissociated at very low exposures as evident by the appearance of the atomic-oxygen species only. In addition to the enhancement of the sticking coefficient of molecular oxygen and to its dissociation, the cesium is also found to promote oxidation by weakening the surface atom back bonds as in the case of silicon.[7]

The Cs $5p$ semicore levels (as Cs $4d$ core levels[13]) are shifted to lower binding energies by 0.3 eV (Fig. 2). Much larger shifts (0.75–1.5 eV) to lower binding energies have been observed on transition metals,[12] where oxygen reacts both with the metal surface and the cesium. This confirms that, on indium phosphide, oxygen reacts more strongly with the substrate than with the promoting cesium adsorbate.

Further evidence of the importance of the molecular-

oxygen dissociation by the catalyst was obtained by comparing the effect of cesium with that of sodium on the same InP(110) surface. In the presence of a sodium monolayer and in strong contrast with cesium, there is no phosphorous $2p$ chemically shifted peak corresponding to phosphates for molecular-oxygen exposures between 0.25 and 116 L. The absence of catalytic activity for sodium (even above an exposure of 100 L) is rather puzzling since both Cs and Na, as well as K, have similar effects on the oxidation of silicon.[6,7] As with cesium, the In $4d$ core level does not exhibit any significant changes with oxygen exposures.[13]

Valence-band spectra from the sodiated InP(110) shows the presence of a new broad electronic structure around 6 eV with sodium deposition as observed for the Cs/InP(110) interface (Fig. 2) but with a larger intensity. The nature of this electronic structure is also likely due to a sodium-induced interface state. A similar peak was also observed both on Cs/GaAs and K/GaAs systems where, interestingly, the state induced by potassium (which also has a smaller radius than cesium) is also larger in intensity when compared to the one induced by cesium.[10] We will discuss these points in a forthcoming paper. The exposition to molecular oxygen of the Na/InP(110) interface shows that oxygen remains in the molecular form as evident from the oxygen $2p$ level (peak A, Fig. 3) but not in the dissociated one. This indicates that like cesium, sodium increases the oxygen sticking coefficient dramatically. However, in contrast to Cs, Na does not dissociate the molecular oxygen at similar exposures. Therefore, this explains the absence of electronic promotion and further confirms that the dissociation plays a central role in the mechanism of promotion.

The above results provide new insight at the atomic scale into the role of alkali metals for the oxidation of the InP(110) surface. However, interesting new questions arise, such as why cesium and sodium behave differently. This point appears even more puzzling since both Na/Si and Cs/Si interfaces have been found to have the same basic electronic properties, and to enhance the oxidation rate of silicon (the onset of oxidation was 2 L of oxygen for either one monolayer of Cs or Na) on Si(100)2×1.[6,7] Furthermore, Chang *et al.*[14] recently found evidence of the catalytic activity of sodium in GaAs oxidation at various coverages below as well as above the monolayer. It is therefore reasonable to assume that the absence of oxygen dissociation at the above exposures by the sodium overlayer adsorbed on the InP(110) also involves the nature of the substrate. This behavior could possibly be connected to structural differences. For InP, the indium radius is larger by 30% than the phosphorus one (1.44 instead of 1.10 Å, while for gallium and arsenic, they are about the same (1.26 and 1.18 Å, i.e., 6% difference). Thus the site selectivity as well as the height of the alkali adatom above the surface could be of relevance.

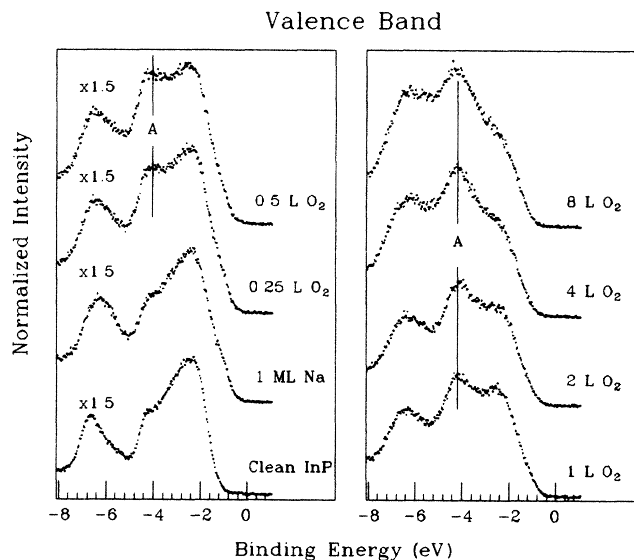

FIG. 3. Valence-band spectra of O_2/1 ML Na/InP(110) for molecular-oxygen exposures between 0.25 and 8 L. The photon energy was 82 eV. The Fermi level of the clean InP(110) surface covered with a sodium monolayer is chosen as reference for the binding energies.

In conclusion, we have shown the crucial role of the oxygen dissociation in the process of catalytic oxidation by alkali metals. In contrast with Cs adsorbed on transition-metal surfaces, a precursor oxygen molecular state exists on the cesiated InP(110) surface. The dissociation of this precursor molecular state occurs at a critical oxygen exposure corresponding to the onset of oxide formation. During oxide growth, both precursor and dissociative states coexist, which implies a dynamic equilibrium between molecular and atomic oxygen. Most significantly, the cesium overlayer was found to dramatically enhance the indium phosphide oxidation rate by 13 orders of magnitude, which is the largest catalytic promotion effect ever observed for a semiconductor.

We thank the technical staff of the Synchrotron Radiation Center of the University of Wisconsin–Madison. This work was supported by the National Science Foundation under Grant No. 84-05173 through Northern Illinois University.

*Permanent address: Commissariat à l'Energie Atomique, Service de Physique des Atomes et des Surfaces, CEN-Saclay, 91191 Gif-sur-Yvette Cédex, France.

†Mailing address.

‡Present address: Deacon Research, 900 Welch Road, Palo Alto, CA 94304.

[1]See, e.g., review articles by L. W. Wilmsen, J. Vac. Sci. Technol. **19**, 279 (1981) or H. H. Wieder, *ibid.* A **2**, 97 (1984).

[2]K. A. Bertness, T. Kendelewicz, R. S. List, H. O. Williams, I. Lindau, and W. E. Spicer, J. Vac. Technol. A **4**, 1424 (1986).

[3]G. Hollinger, G. Hughes, F. J. Himpsel, F. Houzay, J. L. Jordan, and J. F. Morar, Surf. Sci. **168**, 617 (1986).

[4]G. Hughes and R. Ludeke, J. Vac. Sci. Technol. B **4**, 1109 (1986).

[5]See, e.g., J. Derrien and F. Ringeisen, Surf. Sci. Lett. **124**, L235 (1983); A. Franciosi, S. Chang, P. Philip, C. Caprile, and J. Joyce, J. Vac. Sci. Technol. A **3**, 933 (1985); S. Chang, P. Philip, A. Wall, A. Raisanen, N. Trouillier, and A. Franciosi, Phys. Rev. B **35**, 3013 (1987) F. U. Hillebrecht, M. Ronay, D. Rieger, and F. J. Himpsel, *ibid.* **34**, 5377 (1986), and references therein.

[6]P. Soukiassian, T. M. Gentle, M. H. Bakshi, and Z. Hurych, J. Appl. Phys. **60**, 4339 (1986).

[7]P. Soukiassian, M. H. Bakshi, Z. Hurych, and T. M. Gentle, Phys. Rev. B **35**, 4176 (1987); H. I. Starnberg, P. Soukiassian, M. H. Bakshi, and Z. Hurych, *ibid.* **37**, 1315 (1988).

[8]W. E. Spicer, I. Lindau, C. Y. Su, P. W. Chye, and P. Pianetta, Appl. Phys. Lett. **33**, 934 (1978); J. Derrien, these de Doctorat d'Etat es Sciences Physiques, Université d'Aix-Marseille, 1976.

[9]P. Soukiassian, M. H. Bakshi, and Z. Hurych, J. Appl. Phys. **61**, 2679 (1987).

[10]C. M. Beronit, C. Calandra, C. Mariani, and S. Valeri (unpublished).

[11]U. Hofer, P. Morgen, W. Wurth, and E. Umbach, Phys. Rev. Lett. **55**, 2979 (1985).

[12]P. Soukiassian, P. Roubin, J. Cousty, R. Riwan, and J. Lecante, J. Phys. C **18**, 4785 (1985); P. Soukiassian, R. Riwan, Y. Borensztein, and J. Lecante, *ibid.* **17**, 1761 (1984).

[13]M. H. Bakshi, P. Soukiassian, H. Starnberg, A. S. Bommannavar, and Z. Hurych (unpublished).

[14]S. Chang, P. Philip, A. Wall, A. Raisanen, N. Trouillier, A. Franciosi, and P. Soukiassian (unpublished).