

The dependence of the oxidation enhancement of InP(100) surface on the coverage of the adsorbed Cs

Yun Sun^{a)}, Zhi Liu and Piero Pianetta

Stanford Synchrotron Radiation Lightsource, Menlo Park, California 94025, USA

We report the oxidation of the InP(100) surface promoted by adsorbed Cs by synchrotron radiation photoemission. Oxygen exposure causes reduction of the charge transferred to the InP substrate from Cs and the growth of indium oxide and phosphorous oxide. The oxide growth displays a clear dependence on the Cs coverage. The oxidation of phosphorous is negligible up to 1000 L of O₂ exposure when the Cs coverage is less than half a monolayer (ML), but the formation of the second half monolayer of Cs greatly accelerates the oxidation. This different enhancement of the InP oxidation by the first and the second half monolayer of Cs is due to the double layer structure of the adsorbed Cs atoms, and consequently the higher 6s electron density in the Cs atoms when Cs coverage is larger than 0.5 ML.

^{a)} Author to whom correspondence should be addressed. Electronic mail: ssun@slac.stanford.edu.

I. Introduction

GaAs has been extensively studied in negative electron affinity (NEA) photocathode applications.¹ The current generation of night vision devices, utilizing GaAs NEA photocathodes to detect the IR emission from targets, has limited range and resolution. IR laser beam illumination of targets provides an effective solution for longer detection range and better image resolution. However, the wavelength of the IR laser beam has to be long enough so that damages to human eyes can be avoided. This requirement for long wavelength IR sensitivity has driven the development of smaller band gap $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ materials. Adjusting the ratios between different elements in those materials can change the band gap to match specific wavelength requirements. However, those band engineered materials cannot achieve NEA by themselves so they need a lattice matched InP layer as an efficient electron emission surface.² InP can provide an NEA surface after being activated by Cs and O_2 , following the standard activation procedure developed for III-V semiconductors.¹ The activation procedure involves a Cs deposition step first followed by alternating steps of Cs+ O_2 co-deposition and Cs alone deposition until the quantum efficiency (Q.E.) is maximized. The activation process builds up several monolayers (ML) of Cs and oxygen on the surface. The enhanced oxidation of the InP substrate due to the presence of Cs plays a major role in the degradation of the Q.E. In our vacuum system, the Q.E. of a typical InP photocathode can drop to 10% of its starting value within 24 hours.² The study of this Cs-enhanced oxidation of InP can help the development of InP-based photocathodes and can provide scientific knowledge for further performance improvements. The oxidation study of Cs covered InP is not limited to photocathode applications; it is also of general interest in the

research effort on the catalytic behavior of alkali metals in the enhancement of semiconductor oxidation.³⁻⁶ Most of the earlier publications were focused on the InP(110) cleaved surface, not on the InP(100) surface, which is of practical importance in current photocathodes applications.

In this work, we study the oxidation of InP(100) samples with different Cs coverages by synchrotron radiation photoemission. O₂ exposure reduces the charge transferred from Cs to the InP substrate and causes the oxidation of the surface indium and phosphorous. The oxidation enhancement is significantly higher when the Cs coverage is larger than 0.5 ML. This is consistent with the double layer structure of one monolayer of Cs on the InP(100) surface, in which the Cs atoms retain more 6s electron density in the Cs layer during the formation of the second half monolayer of Cs.⁷

II. Experiment

The InP(100) wafers used were Zn doped, p type with carrier concentrations of $5 \times 10^{17} \text{ cm}^{-3}$ and manufactured by Wafer Technology, UK. They were chemically cleaned by 1 min etch in 9% HCl to remove the surface native oxide and subsequently annealed in our UHV system at 400 °C for 20 min to remove the surface hydrogen termination generated during the HCl etch.⁸ Cs was evaporated from a carefully outgassed SAES Getters dispenser. The deposition rate of Cs was calibrated by monitoring the photocurrent emitted from the InP sample.⁷ Dry O₂ was introduced into the UHV chamber through a leak valve and the pressure was measured by a Pfeiffer cold cathode gauge. Ion gauges were not used during the experiments to avoid the generation of excited oxygen.⁹

Photoemission spectra were collected by a PHI 10-360 hemispherical electron energy analyzer at beam line 8-1 (hv: 30-170 eV) and beam line 10-1 (hv: 200-1200 eV) of Stanford Synchrotron Radiation Lightsource (SSRL). Unless stated otherwise, all spectra were taken at normal emission angle. The Core level spectra were fitted using the program developed by A. Herrera-Gomez,¹⁰ with the spin orbit splitting fixed at 2.28 eV for Cs 4d, 0.855 eV for In 4d, and 0.86 eV for P 2p.

III. Results and Discussions

The Cs 4d and O 1s spectra for an InP(100) sample with 0.6 ML of Cs and dosed with 0.2 – 1000 Langmuir (L) of O₂ are plotted in figure 1(a) and 1(b), respectively. As the O₂ dosage increases, the Cs 4d peak gradually shifts to higher kinetic energy (lower binding energy), a phenomenon observed before on Cs/InP(110) surfaces.^{3,5} When the total O₂ dosage reaches 1000 L, the Cs 4d peak shifts by 0.55 eV. O₂ exposure also causes the oxidation of the InP substrate, which will be discussed in more detail later. At all oxygen exposure levels, the amount of oxygen in the InP substrate oxides, calculated from the oxide components of P 2p and In 4d spectra, only accounts for a small part of the total amount of oxygen, calculated from the intensity of the O 1s spectra. This indicates that a large part of the oxygen is retained in the Cs layer. The line shape of the O 1s peaks indicates that they are composed of at least two components, labeled as O1 and O2 in the numerical fitting of the O 1s spectrum after 1L of O₂ dose. An earlier study of the Cs/O activation layer of InP NEA photocathodes discussed in detail the existence of these two components for O 1s and their assignments.² The component O1 and O2 are attributed to the superoxide ion (O₂⁻) and the peroxide ion (O₂²⁻), which are molecular

oxygen with the π^* anti-bonding molecular orbital filled with one or two additional electrons, respectively.² At high O_2 dosages, the superoxide grows larger relative to the peroxide because of the reaction: $O_2^{2-} + O_2 \rightarrow 2O_2^-$. The O 1s spectra should also contain a small contribution from the InP substrate oxide but the insufficient peak separation prevents an easy deconvolution of the substrate oxide component.²

The existence of the ionic O_2^{2-}/O_2^- , also called molecular-oxygen precursor in some earlier publications,⁵ offers an explanation for the Cs 4d peak shift when the sample is exposed to O_2 . The direction of the shift is at first counter-intuitive because if Cs atoms lose electrons to oxygen, we expect Cs 4d to move to lower kinetic energy (higher binding energy). It actually moves to higher kinetic energy because of the Coulombic interaction between the Cs 4d core holes and the negative charged O_2^{2-}/O_2^- ions in the Cs/O layer.^{12, 13} This Madelung potential effect causes the Cs core levels to shift to higher kinetic energy, as commonly observed in ionic compounds of Cs.¹⁴

Earlier studies on the oxidation of the InP(110) surface already clearly demonstrated the catalytic behavior of Cs during the oxidation.³⁻⁶ In this study, we detect no oxide on clean InP(100) surfaces with O_2 exposure up to 10^5 L, but the adsorbed Cs atoms on the surface greatly enhance the oxidation of the InP(100) substrate. The In 4d spectra with their numerical fitting for the InP sample with 0.6 ML of Cs and dosed with 0 L, 0.4 L, 1 L and 1000 L of O_2 are plotted in figure 2(a), 2(b), 2(c), and 2(d), respectively. In figure 2(a), the Cs induced component is labeled as In(Cs) on the higher kinetic energy side of the bulk peak. This component is due to the charge transfer from the adsorbed Cs atoms to the InP substrate.⁷ O_2 introduction reduces this Cs induced component and it eventually disappears when O_2 dosage reaches 1000 L. This reduction

of In(Cs) is a result of the loss of electrons to O₂.¹⁵ In the mean time, a component with a chemical shift of 0.45 ± 0.05 eV at the lower kinetic energy side of the bulk peak appears and keeps growing with O₂ dosing. This component is due to the oxidized surface indium,⁸ and the coverage is estimated to be 0.3 ± 0.1 ML at 1000 L of O₂ dose.

The Cs induced P 2p component, labeled as P(Cs), in the P 2p spectra plotted in figure 3(a)-(d), decreases by O₂ exposure. This decrease of P(Cs) component also demonstrates the reduction of the charge transferred from the adsorbed Cs to the InP substrate. However, the oxidation of phosphorous happens much later than the oxidation of indium. While the indium oxide is already observable at 0.4 L of O₂ exposure (figure 2(b)), the oxide peak of P 2p is barely detectable at 1 L of O₂ exposure, as shown in figure 3(c). At this early stage of the oxidation, oxidation seems to happen almost exclusively on surface indium. This is different from earlier oxidation studies on the Cs/In(110) surface, where both surface indium and phosphorous were believed to be oxidized simultaneously and the form of oxide was believed to be InPO₄.^{4,5} This difference may stem from the different atomic structure of the InP(100) and the In(110) surfaces. On InP(110) surfaces, both indium and phosphorous atoms are exposed and oxygen can have easy access to both the surface indium and the surface phosphorous. For our clean InP(100) samples, as shown in our earlier work, indium terminates the surface, and thus the top layer of phosphorous atoms are below the indium termination.⁸ In order to oxidize the phosphorous atoms, oxygen atoms have to break the In-P back bonds. This indium-on-top structure is the reason that during the Cs deposition, the adsorbed Cs atoms transfer charge to the surface indium atoms first.⁷ Similarly, due to this indium-on-top structure on InP(100), oxygen oxidizes the surface indium first and leaves the In-P

back bonds mostly intact in the initial stage of oxidation. When more O₂ is introduced onto the surface, surface phosphorous starts to be oxidized and as illustrated in figure 3(d), 0.4 ± 0.1 ML of phosphorous oxide is eventually formed when O₂ exposure reaches 1000 L.

We also carried out the oxidation study on InP(100) samples covered with 0.2 ML, 0.5 ML and 1 ML of Cs. Most of the observations are similar to the InP(100) sample with 0.6 ML of Cs, such as the shift of the Cs 4d peak to higher kinetic energy, the existence of O₂²⁻/O₂⁻, the reduction of the charge transferred from the Cs atoms to the InP substrate, and the oxidation happening first on surface indium. However, the degree of oxidation of the InP(100) surfaces greatly depends on the Cs coverage. The In 4d and P 2p spectra for InP(100) samples with different Cs coverages and then dosed with 1000 L of O₂ are plotted in figure 4(a) and 4(b), respectively. More Cs on the surface clearly leads to higher degree of oxidation. Examination of the P 2p spectra also reveals a large contrast between the samples with 0 - 0.5 ML of Cs and those with more than 0.5 ML of Cs. When the Cs coverage is below (or equal to) 0.5 ML, phosphorous oxide is barely detectable, even with a O₂ exposure up to 1000 L. Increasing the Cs coverage by only 0.1 ML, from 0.5 ML to 0.6 ML, leads to significant phosphorous oxide formation. This observation can better be illustrated by plotting the oxide/bulk peak ratio as a function of the Cs coverage for samples dosed with 1000 L of O₂, as shown in figure 5. In figure 5, the ratios for In 4d carry error bars because the individual In 4d components are very close to each other so the fitting results are sensitive to the initial fitting parameters and consequently less accurate. As shown in figure 5, before the Cs coverage reaches 0.5 ML, oxidation mainly happens on the surface indium due to the indium-on-top nature of the

InP(100) surface. Significant oxidation of phosphorous takes place when the Cs coverage is above 0.5 ML. The indium oxide growth is also noticeably faster when the Cs coverage is above 0.5 ML. The oxidation of the InP(100) surfaces with more than 0.5 ML of Cs shows a totally different dependence on the Cs coverage compared with the surfaces with no more than 0.5 ML of Cs.

From the earlier extensive studies of the alkali metal promoted oxidation of semiconductor surfaces, the roles of Cs are summarized as: increasing the O₂ sticking coefficient; filling the empty surface dangling bonds with Cs 6s valence electrons; weakening back bonds; and assisting in the dissociation of O₂ molecules by filling the anti-bonding orbital.^{4, 15} Based on the O 1s and Cs 4d intensities after the samples are exposed with 1000 L of O₂, we estimate the atomic ratio of O/Cs to be 3 ± 1 for all the Cs coverages investigated in this study, regardless of whether the coverage is below or over 0.5 ML. This means that the amount of O₂ retained on the Cs/InP(100) surface has a approximately linear relationship with the amount of Cs. There is no obvious change in O₂ sticking coefficient. Therefore, the possible change of O₂ adsorption is an unlikely reason for the change of the oxidation dependence on the Cs coverage when it goes above 0.5 ML. The filling of the empty surface dangling bonds and the weakening of the back bonds are direct consequences of the charge transfer from the adsorbed Cs to the InP substrate. According to the earlier study of the Cs deposition on the InP(100) surface, most of the charge transfer from the Cs atoms to the InP substrate occurs before the first half monolayer is completed, and only a very small amount of additional charge transfer takes place during the formation of the second half monolayer of Cs.⁷ Therefore, the filling of the dangling bonds and the weakening of the back bonds are not likely to

account for such a sudden increase of the InP oxidation when the Cs coverage is above 0.5 ML either.

A previous Cs/InP(100) study established that the monolayer of Cs on InP(100) surface has a double layer structure with the second half monolayer located above the first half monolayer.⁷ Based on this Cs/InP(100) study, figure 6 shows a schematic side-view of adsorbed Cs atoms on InP(100) surface. As shown in the figure, the Cs atoms in the second half monolayer, not in direct contact with the InP(100) substrate, contribute little charge to the InP substrate so the Cs atoms keep more of their 6s valence electrons and behave more like metallic Cs.⁷ This conclusion is consistent with the observation of higher Cs 6s density in the Cs layer at high Cs coverages by Nishigaki on Cs/GaAs(100) surface, utilizing metastable deexcitation spectroscopy (MDS).¹⁶ Those electron rich Cs atoms in the second half monolayer can readily give up their 6s valence electrons to the adsorbed O₂ molecules to fill their π^*_{2p} anti-bonding orbital, which weakens the O-O bonds and makes the molecular O₂ easy to dissociate. When the Cs coverage is below 0.5 ML, since the Cs atoms already donate a lot of charge to the InP(100) substrate, they are less efficient in filling the O₂ π^*_{2p} orbital. The InP surface dangling bonds, when filled with electrons provided by the adsorbed Cs atoms, are generally believed to participate in the filling of O₂ π^*_{2p} states, too.^{6, 15} Since those dangling bonds states obtain their electrons from Cs, they hold the electrons more tightly, and thus are less willingly to lose electrons to O₂ molecules than neutral Cs atoms. Therefore, we believe that the sudden increase of the InP(100) substrate oxidation is caused by the higher Cs 6s electron density retained by the Cs atoms when the second half monolayer of Cs starts to form. It is much easier for those electron-rich Cs atoms at coverages over 0.5 ML to provide electrons to

fill the O₂ anti-bonding orbital, as compared to the Cs atoms at coverages below 0.5 ML or the filled surface dangling bonds. Consequently, the presence of electron-rich Cs atoms in the second half monolayer greatly facilitates the dissociation of O₂ molecules and enhances the oxidation of the InP substrate. This difference in valence electron density at different Cs coverages is probably also the reason for the onset, at 0.5 ML of Cs coverage, of promoted oxidation observed on several other semiconductor surfaces such as Si(100), Si(111) and InP(110) surfaces, which was discussed in ref. 6 and the publications referenced within.

IV. Conclusions

We studied the oxidation of InP(100) samples with different Cs coverages. O₂ adsorption on Cs/InP(100) surfaces reduces the charge transferred from the Cs atoms to the InP(100) substrate and causes the oxidation of the InP(100) surface. The growth of indium oxide precedes the growth of phosphorous oxide because indium terminates the clean InP(100) surface so oxygen has to break the In-P back bonds to oxidize phosphorous. With no more than 0.5 ML of Cs, the oxidation of phosphorous is negligible after the sample is exposed with 1000 L of O₂. The oxidation is greatly enhanced when the Cs coverage is above 0.5 ML. This is because that Cs atoms have a higher 6s electron density at coverages above 0.5 ML. This higher 6s electron density makes the filling of the O₂ molecule anti-bonding orbital and the subsequent dissociation of O₂ much easier. This enhancement of InP(100) oxidation by the presence of Cs is one of the major reasons for the Q.E. decay of the InP based photocathodes activated by Cs

and O₂. Therefore, a different gas agent may be considered to replace O₂ in the activation process if this problem needs to be avoided.

Acknowledgements

This research was funded by Army Contract No. DAAD19-02-1-0396 and was carried out at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

References:

- ¹ R. L. Bell, *Negative Electron Affinity Devices* (Clarendon, Oxford, 1973).
- ² Y. Sun, Z. Liu, P. Pianetta, and D. Lee, *J. Appl. Phys.* **102**, 074908 (2007).
- ³ W. E. Spicer, I. Lindau, C. Y. Su, P. W. Chye, and P. Pianetta, *Appl. Phys. Lett.* **33**, 934 (1978).
- ⁴ P. Soukiassian, M. H. Bakshi, and Z. Hurych, *J. Appl. Phys.* **61**, 2679 (1987).
- ⁵ P. Soukiassian, M. H. Bakshi, H. I. Starnberg, A. S. Bommannavar, and Z. Hurych, *Phys. Rev. B.* **37**, 6496 (1988).
- ⁶ H. I. Starnberg and P. Soukiassian, M. H. Bakshi and Z. Hurych, *Surf. Sci.* **224**, 13 (1989).
- ⁷ Y. Sun, Z. Liu, and P. Pianetta, *J. Vac. Sci. Technol. A* **25**, 1351 (2007).
- ⁸ Y. Sun, Z. Liu, F. Machuca, P. Pianetta, and W. E. Spicer, *J. Appl. Phys.* **97**, 1 (2005).
- ⁹ P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, *Phys. Rev. B* **18**, 2792 (1978).
- ¹⁰ A. Herrera-Gomez, F. S. Aguirre-Tostado, Y. Sun, P. Pianetta, Z. Yu, D. Marshall, R. Droopad, and W. E. Spicer, *J. Appl. Phys.* **90**, 6070 (2001).
- ¹¹ T. Kendelewicz, P. Soukiassian, M. H. Bakshi, Z. Hurych, I. Lindau, and W. E. Spicer, *J. Vac. Sci. Technol. B* **6**, 1331 (1988).
- ¹² P. A. Schultz and R. P. Messmer, *Surf. Sci.* **209**, 229 (1989).
- ¹³ K. Yamada, J. Asanari, M. Naitoh, and S. Nishigaki, *Surf. Sci.* **402**, 683, (1998)
- ¹⁴ *Handbook of X-Ray Photoelectron Spectroscopy*, edited by J. Chastain (Perkin-Elmer Corporation, Physical Electronics Division, 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344, 1992).
- ¹⁵ B. Hellsing, *Phys. Rev. B* **40**, 3855 (1989).

¹⁶S. Nishigaki, K. Yamada, J. Asanari, and M. Naitoh, *Ultramicroscopy* **73**, 223 (1998)

Figure Captions:

Figure 1. (a) Cs 4d and (b) O 1s spectra for a InP(100) sample with 0.6 ML of Cs on the surface dosed with 0.2 L – 1000 L of O₂.

Figure 2. In 4d spectra for a InP(100) sample with 0.6 ML of Cs on the surface dosed with (a) 0L, (b) 0.4L, (c) 1L, and (d) 1000L of O₂. The dots are the experimental data and the lines are the numerical fitting.

Figure 3. P 2p spectra for a InP(100) sample with 0.6 ML of Cs on the surface dosed with (a) 0L, (b) 0.4L, (c) 1L, and (d) 1000L of O₂. The dots are the experimental data and the lines are the numerical fitting.

Figure 4. (a) In 4d and (b) P 2p spectra for InP(100) samples with 0.2, 0.5, 0.6, 1.0 ML of Cs dosed with 1000 L of O₂.

Figure 5. The ratios between the oxide peak and the bulk peak for In 4d and P 2p as a function of Cs coverage for InP(100) samples dosed with 1000 L of O₂.

Figure 6. Schematic side view of the Cs atoms on the InP(100) substrate. The Cs atoms in the first half monolayer are positive charged after they donate their 6s electrons to the InP substrate. The Cs atoms in the second half monolayer retain their 6s electrons and are readily to give up the electrons to O₂. The filling of O₂ anti-bonding molecular orbital facilitates the dissociation of O₂ and the oxidation of the InP substrate.

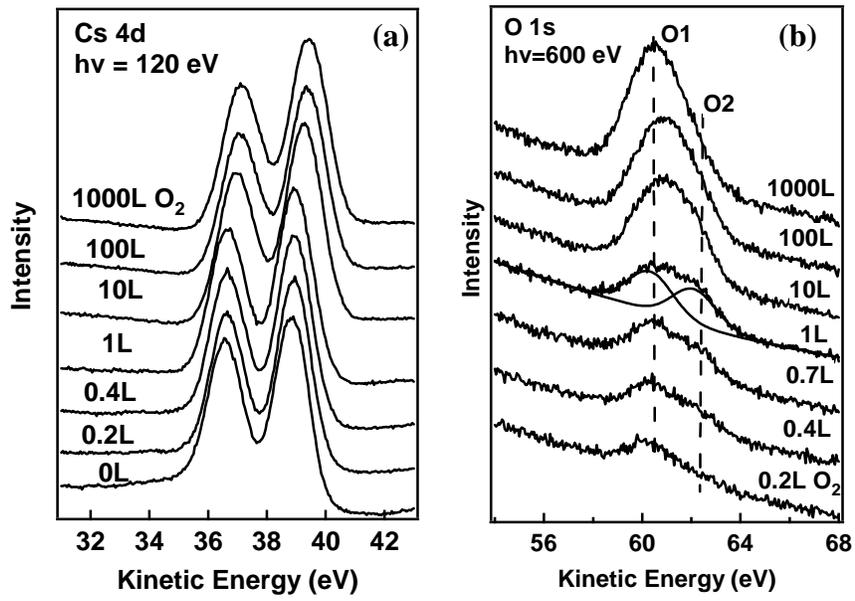


Figure 1.

Y. Sun, et al. JAP

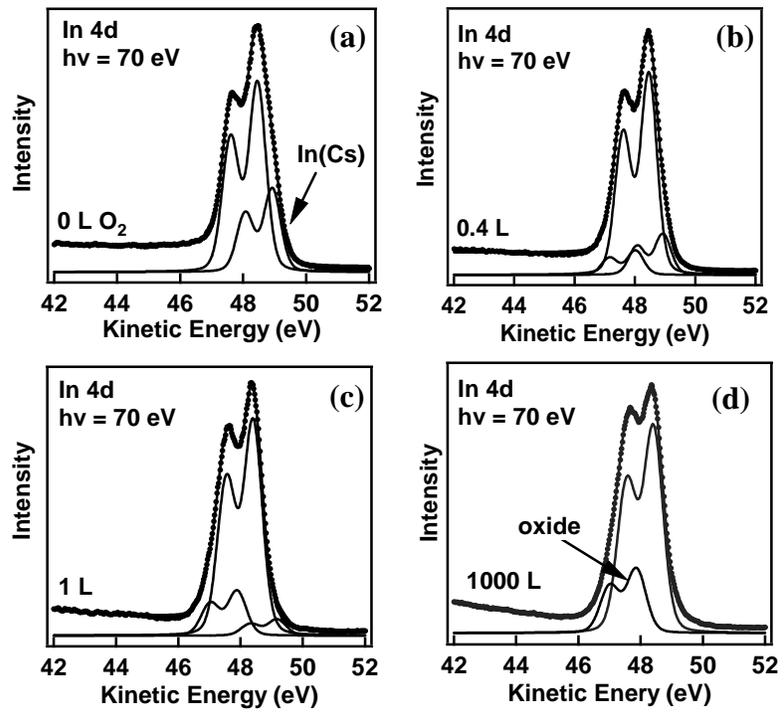


Figure 2.

Y. Sun, et al. JAP

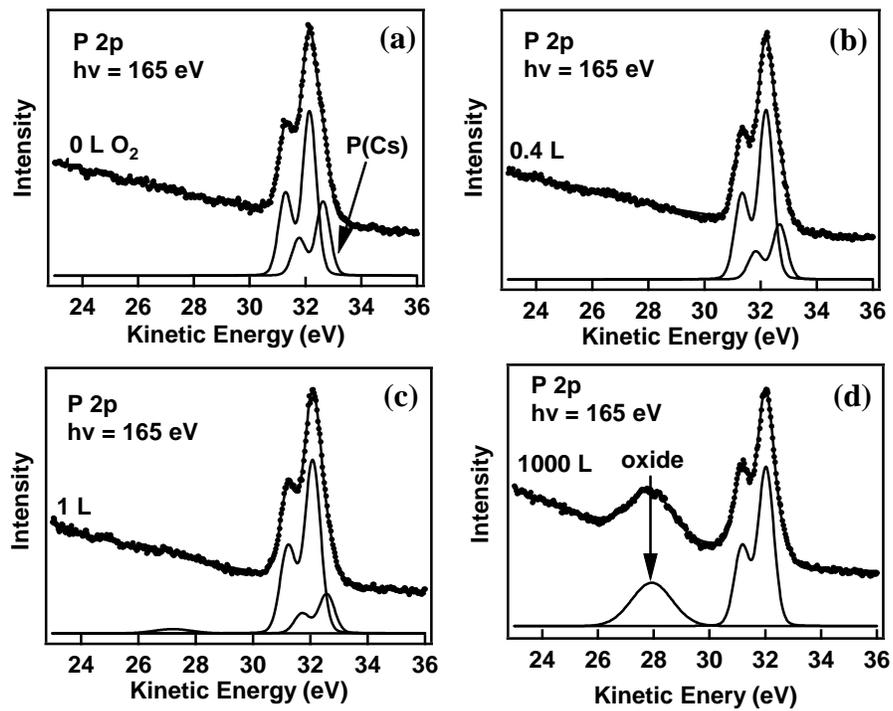


Figure 3.

Y. Sun, et al. JAP

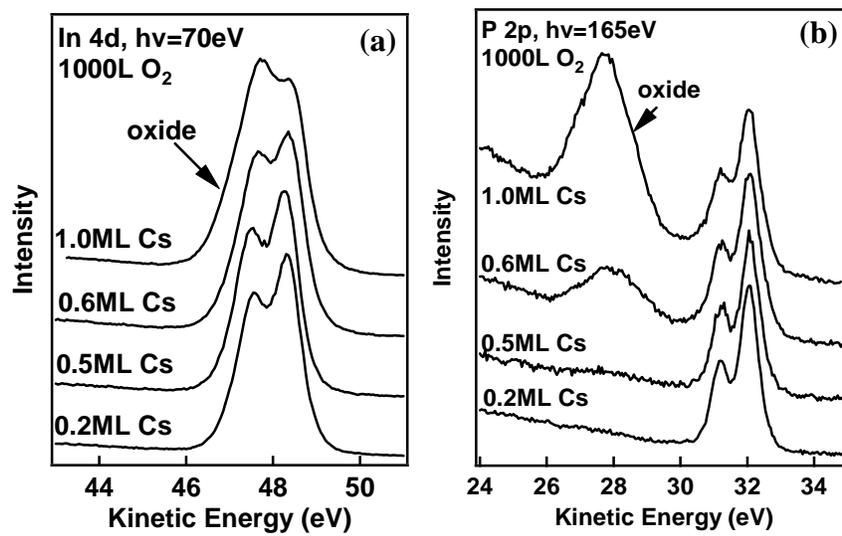


Figure 4.

Y. Sun, et al. JAP

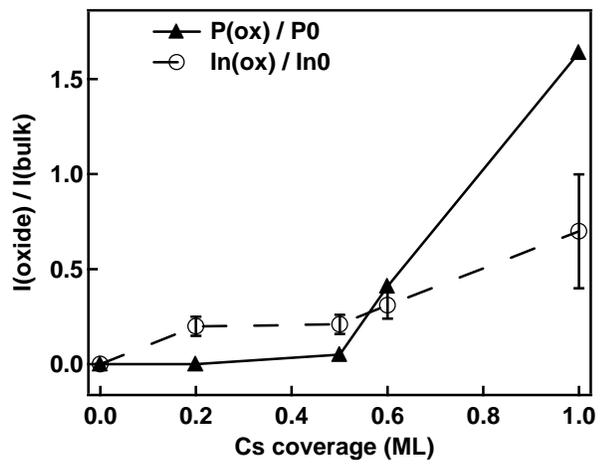


Figure 5.

Y. Sun, et al. JAP

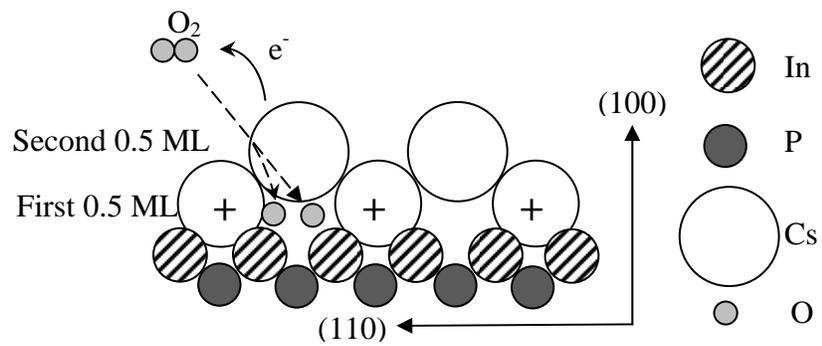


Figure 6.

Y. Sun, et al. JAP