

**Formation of Cesium Peroxide and Cesium Superoxide on InP Photocathode
Activated by Cesium and Oxygen**

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Abstract:

Activation of p type III-V semiconductors with Cesium and Oxygen has been widely used to prepare Negative Electron Affinity (NEA) photocathodes. However, the nature of the chemical species on the surface after the activation is not well-understood. In this study, InP NEA photocathodes activated with Cesium and Oxygen are studied using Synchrotron Radiation Photoelectron Spectroscopy, also called photoemission. Based on the O1s core level as well as the valence band spectra, Cs peroxide and Cs superoxide are identified on the InP surface. Transformation from Cs peroxide to Cs superoxide is observed after the activation, and probably is the major reason for the decay of the Quantum Yield of the photocathode. The oxidation of the InP substrate is also observed with the elapse of time, adding to the decay of the Quantum Yield.

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1. Introduction:

The performance requirements of photocathodes for infrared imaging devices have driven the development of Negative Electron Affinity surfaces using III-V semiconductors. Such surfaces are created by the deposition of Cs and O on III-V surfaces which results in a lowering of the work function below the bulk conduction band minimum thus allowing the direct emission of electrons at the bottom of the conduction band into vacuum [1, 2]. The Cs+O / GaAs system has received the most attention during the past several decades and different models describing the origin of the NEA condition have been suggested [1-17]. One of the most important pieces of information for people to understand the NEA surfaces is the chemical composition of the surface Cs/O layer. However, despite the importance, the nature of the surface oxides after activation is still not well understood.

Although InP alone does not produce a better NEA surface than GaAs, recent requirements for 1.54 micron photocathodes has driven the development of $Ga_xIn_{1-x}As_yP_{1-y}$ band engineered materials with band gaps small enough to detect the long wavelength IR radiation. However, this band gap is too small for the creation of an efficient NEA surface. Fortunately, these materials can be lattice matched to InP, which can be treated with Cs and O to create an efficient NEA surface. The physics and chemistry of the InP surface is very similar to that of GaAs so that the results obtained here should have general applications. In addition, the relatively large spin-orbit splittings of the In4d and P2p core levels allow better identification of surface chemical shifts

caused by the interactions between Cs / O and the InP substrate. Therefore, InP has allowed us to better understand the mechanism of NEA formation.

In this work, we studied the activation of InP by Cs and O. A good activation can achieve 12% of quantum yield in the reflection mode. Cs peroxide and Cs superoxide are identified on the surface after the activation. The Cs+O / InP is not a chemically stable system when residual oxygen is present. Quantum yield decay is observed following the activation, and this decay is accompanied by a change of Cs oxide as well as the oxidation of the InP substrate.

2. Experimental:

The InP(100) wafers used are Zn doped, p-type with carrier concentrations of $5 \times 10^{17} \text{ cm}^{-3}$. They were mirror-finished and manufactured by Wafer Technology, U.K..

Chemical cleaning process described in our earlier work [18] is used to obtain a clean starting InP(100) surface. The sample is first etched in 4:1:100 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution for 2 minutes, rinsed with DI water and then etched in 1:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ solution for 30 s, resulting in a oxide free, hydrogen terminated surface. It is then transferred into the photoemission chamber and annealed 330°C for half an hour to obtain a clean InP surface.

The deposition of Cs is done from SAES Getters (Italy) chromate source. Oxygen was introduced into the chamber through a leak valve. During the Cs and O co-deposition, the pressure of O_2 is controlled to be less than 10^{-8} torr.

A 0.95 mW He-Ne laser ($\lambda = 632.8$ nm) is used as the light source to monitor the activation process and also to measure the quantum yield. The number of photons from the laser is measured by a calibrated Si photodiode. Photoelectrons emitted from the InP photocathode are collected by a biased wire. The work function of the sample can be calculated from the low energy cut off of the photoemission energy distribution curve.

Experiments are performed at beam line 8-1 (photon energy range of 30-190 eV) and beam line 8-2 (photon energy range of 200-1300 eV) at Stanford Synchrotron Radiation Laboratory (SSRL). The photon energy range of beam line 8-1 gives the best combination of surface sensitivity and energy resolution for the In 4d ($E_b = 16.5$ eV), P 2p ($E_b = 135$ eV) and Cs4d ($E_b = 78$ eV) core levels and the valence band which are measured at $h\nu = 70, 165, 120$ and 70 eV, respectively. Beam Line 8-2 must be used to access the O1s level ($E_b = 543.1$ eV) and also to monitor the carbon contamination by looking at C1s ($E_b = 284.2$ eV).

The photoemission spectra are collected at normal emission angle with a PHI (model 10-360) spherical energy analyzer with a multi-channel detector. The spectra are fitted with Voigt functions, which are Gaussian broadened Lorentzian line shapes. The spin-orbit splitting is fixed at 0.86eV for P 2p, 0.855eV for In 4d and 2.28eV for Cs4d.

3. Results and discussions

3.1. Cs/O activation of InP(100)

In our experiments, the well-known method which involves alternating steps of pure Cs and Cs + O co-deposition steps is used for the activation [19]. The behavior of

one typical activation curve is shown in figure 1 (a) and described below. The quantum yield reaches a maximum with Cs deposition first, which corresponds to 0.5 ML of Cs coverage [26], and then the quantum yield begins to drop. The oxygen is turned on and the pressure is kept around 1×10^{-8} torr. The quantum yield rises first and when it drops, the oxygen is turned off. The quantum yield rises again with Cs alone deposition, and the cycle is repeated for several times until no further improvement of quantum yield can be obtained. If we assume the Cs sticking coefficient is constant during the activation, the total amount of Cs can be estimated as 1.06 ML, and the total oxygen dosage is about 0.94 L.

Another activation curve when O_2 pressure is kept around 2×10^{-9} torr is shown in figure 1 (b). Again the quantum yield reaches the first maximum at about $t = 420$ s, when 0.5 ML of Cs is deposited. Then the oxygen is turned on, the quantum yield keeps increasing until a second maximum is reached after 1000s. Additional tweaking of Cs and oxygen fluxes can not increase the quantum yield, which means that the optimum quantum yield is already achieved. After the activation, the total Cs coverage is estimated as 1.25 ML, and the total oxygen dosage is about 1.24 L.

The activation process is repeated for several times, and a quantum yield of 8%-12 % is achieved routinely. The work function of an activated InP photocathode is around 1.24 ± 0.05 eV, from which the electron affinity is calculated as -0.06 ± 0.05 eV. The amount of Cs is between 1 and 1.5 ML and total oxygen dosage is about 0.9 to 1.7 L. Whether we do activation as shown in figure 1 (a) or in figure 1 (b), the quantum yield and the O / Cs ratio agree very well and there are no significant differences for the

photoemission spectra taken after the activation. This indicates that the total Cs to oxygen ratio is essential for the activation of an InP photocathode.

3.2. Surface chemical species after activation

It is known that Cs and O form several different kinds of oxides [20]. To determine what kinds of oxides exist in the Cs/O layer on InP photocathode surface, we need to examine O1s core level and valence band spectra, as shown in figure 2 (a) and (b). Two distinct O1s components are obvious in O1s spectrum. The component labeled as O1 has a binding energy about 65.1 eV and the component labeled as O2 has a kinetic energy of 62.6 eV. Existence of two components clearly indicates that there are two different oxygen species. Chemistry of Cs tells us that instead of Cs oxide (Cs_2O), Cs peroxide (Cs_2O_2) and Cs superoxide (CsO_2) are the most stable oxides of Cs because the large size of Cs atoms [20], so they are probably the oxides we see in O1s spectrum. However, to make correct assignment of those two peaks, we need to analyze the valence band spectra and compare them with the existing literature [20-25].

Several groups have studied the interaction of bulk Cs with oxygen at low temperatures by carefully examining the valence band spectra [20, 23-25]. Despite some small differences between different publications, it is generally agreed that Cesium peroxide (Cs_2O_2) has three features in the valence band with binding energy about 3.3eV, 6.1eV and 7.5eV, which corresponds to π_{2p}^* , π_{2p} and σ_{2p} molecular orbital for O_2^{2-} , respectively. Cesium superoxide (CsO_2) has four features with binding energy of 4.7eV, 5.8eV, 6.2eV, 8.5eV, the first two of which are from π_{2p}^* orbital of O_2^- , and the third and fourth are from π_{2p} and σ_{2p} , respectively. There are two features for $\text{O}_2^- \pi_{2p}^*$ orbital

because there are two final states after one electron is ionized from this orbital. An energy difference exists for the superoxide peaks between Su's [24] and Woratschek's work [23] but the separations between different superoxide peaks are almost the same. This was attributed to the fact that O_2^{2-} is more affected by the environment because the two π^*_{2p} orbital are not filled.

In the valence band of our InP sample as shown in figure 2(b), there are three prominent features labeled as A, B, D and a clear shoulder labeled as C. Using the calibrated Fermi level as the reference, the binding energy of the peak A, B, C and D is 3.3eV, 5.2eV, 6.8eV and 9.1eV, respectively. By comparing those peaks with the literature mentioned above, we can assign peak A, B, D assigned as π^*_{2p} state of O_2^{2-} , π^*_{2p} state of O_2^- and σ_{2p} of O_2^- , respectively. Other features (6.1eV and 7.5eV O_2^{2-} , 5.8eV and 6.2eV for O_2^-) can not be resolved very well and peak C probably has their combined contributions. The superoxide peaks B and D have an energy difference of about 0.6eV from Su's work [24], but the peak separation matches fairly well. This energy difference is probably caused by the different environment between the thin oxide layer in our study and the bulk oxide in Su's work, as explained earlier. A GaN sample activated with Cs and O also has a very similar but better resolved valence band [26]. Evidence of superoxide CsO_2 formation during Cs and O co-deposition is also supported by previous NEXAFS studies [21, 22].

With the knowledge that there are Cs peroxide and Cs superoxide in the Cs/O layer, we can assign the component with higher kinetic energy (O2) in O1s core level as oxygen in Cs_2O_2 and the one with lower kinetic energy (O1) as oxygen in CsO_2 , because oxygen in O_2^{2-} is more electron rich, thus with smaller binding energy, which leads to

higher kinetic energy. This assignment can be further supported by the correlation between O1s and VB when we study the change of the surface species with time, discussed in the next section.

P2p, In4d spectra after the activation are shown in figure 3 (a) and 3 (b), respectively. There are three components for P2p core level, the one on the center is the component for P in bulk InP, while the one on the left is oxide and the one on the right is identified as Cs induced component due to the charge transfer from Cs to the InP substrate [27]. Similar assignment is given for In4d core level, but here the In oxide component is located very close to the bulk In component. From both In4d and P2p, we can see that the Cs induced components and oxide peaks co-exist. The thickness of the Cs oxide layer is estimated to be 7 ± 2 Å by checking the attenuation of the substrate core levels after the activation.

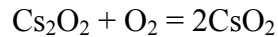
3.3. Decay of Quantum Yield, change of Cs oxide and substrate oxidation

The quantum yield for activated InP(100) decays with time in our vacuum system, which is a direct result of the increase of the work function, as shown in figure 4. For this set of measurements plotted in figure 4, the base pressure of the chamber is 6×10^{-10} torr. However, with a better vacuum, the decay of the quantum yield is slower, which means the rate of decay depends on the pressure of the chamber. To understand the decay, we need to first examine what happens to the surface Cs/O layer as well as the InP substrate after the activation.

Striking changes can be observed in the valence band and O1s spectra, shown in figure 5 (a) and figure 5 (b), respectively. In the valence band, peroxide feature (peak A)

drops down with time; while superoxide features (peak B and peak D) increase. The O1s spectra show the similar behavior, the peroxide peak (O2 component) gets smaller while the superoxide peak (O1 component) becomes larger. The correlation between the changes of Valence band and the changes of O1s core level confirms our earlier assignment of O1 component of O1s core level to CsO₂ and O2 component to Cs₂O₂. Both Valence Band and O1s core level spectra tell us that Cs₂O₂ drops down with time while CsO₂ increases, which indicates that some Cs₂O₂ changes to CsO₂.

Figure 6 shows the O1s / Cs4d ratio, normalized by their ionization cross sections, at hv = 600 eV. Besides the fact that O1 increases and O2 drops, the total O / Cs ratio increases with time. This change is easy to understand because of the oxygen uptake in the reaction for the conversion of Cs₂O₂ to CsO₂:



In this reaction, the Oxygen comes from the environment inside the vacuum chamber. This explains why the quantum yield decays slower with a better vacuum.

The P2p and In4d spectra at different time after the activation are shown in figure 7 (a) and (b), respectively. It can be seen that there is slight increase of P oxide peak, but the In4d line shape change is obvious, which is shown more clearly by the numerical fittings in figure 8. We can see that the Cs-induced In component is reduced with elapse of time and the oxide peak grows. The ratio of the Cs induced and oxide components of In4d and P2p to their bulk peaks are plotted in figure 9. The change of P2p is relatively small compared to In4d. This indicates that most of the oxidation occurs on the In, while most In-P back bonds are intact. This is because the clean InP starting surface prepared in our study is In terminated [18] and the oxidation occurs at room temperature; there is not

enough energy to break the In-P back bonds and cause the further oxidation of phosphorous in InP substrate.

The changes of the InP surface after activation can be summarized as the transformation of Cs peroxide to Cs superoxide and the oxidation of the InP substrate. The decay of quantum yield is very likely caused by those two factors. The transformation of Cs oxide can potentially change the surface dipole strength in an undesirable way. More detailed study of Cs oxide layer will be discussed in later publications [28]. The oxidation of the substrate reduces the effective charge transfer from Cs to InP substrate, as shown by the decrease of Cs induced components in figure 9. This reduction of charge transfer from Cs to the InP substrate causes the reduction of overall dipole, which, in turn, reduces the quantum yield.

4. Conclusions

The activation process of InP(100) by Cs and O is studied. It is found in our study that matching the ratio of Cs to O is the critical factor for obtaining good quantum yield for the InP NEA photocathode. O1s core level tells us that there are two types of oxides in the Cs/O layer after activation. Analysis of the valence band spectra and comparing them with the existing Cs oxidation literature enables us to identify those two oxides as Cs peroxide and superoxide. The Cs oxide / InP interface is unstable when there is residue oxygen around, conversion of Cs peroxide to Cs superoxide and oxidation of the substrate mostly on the In takes place, which leads to the decay of the quantum yield with time.

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Figure Captions

Figure 1. Activation curve for alternating Cs and Cs+O steps. (a) O₂ pressure is about 10⁻⁸ torr, multiple cycles are needed. (b) O₂ pressure is about 2x10⁻⁹ torr, only one cycle is needed.

Figure 2. Photoemission spectra for InP(100) activated by Cs and O. (a) O1s, (b) valence band

Figure 3. Photoemission spectra after the InP(100) sample is activated by Cs and O. (a) P2p, (b) In4d

Figure 4. The decay of the quantum yield and the change of work function for activated InP(100).

Figure 5. (a) Valence Band and (b) O1s core level spectra at different times after the activation of InP(100).

Figure 6. O1s / Cs4d ratio normalized by their cross sections at $h\nu = 600$ eV as a function of time after activation of InP(100) sample. The ratio for O1, O2 and total O are shown.

Figure 7. Photoemission spectra at different times after the InP(100) activation. (a) P2p, (b) In4d

Figure 8. Numerical fittings for In4d spectra at different times after InP(100) activation.

(a) Just after the activation. (b) 3h, (c) 6h, (d) 19.5 h.

Figure 9. The ratio of Cs-induced and oxide components for In4d and P2p to their bulk peaks as function of time.

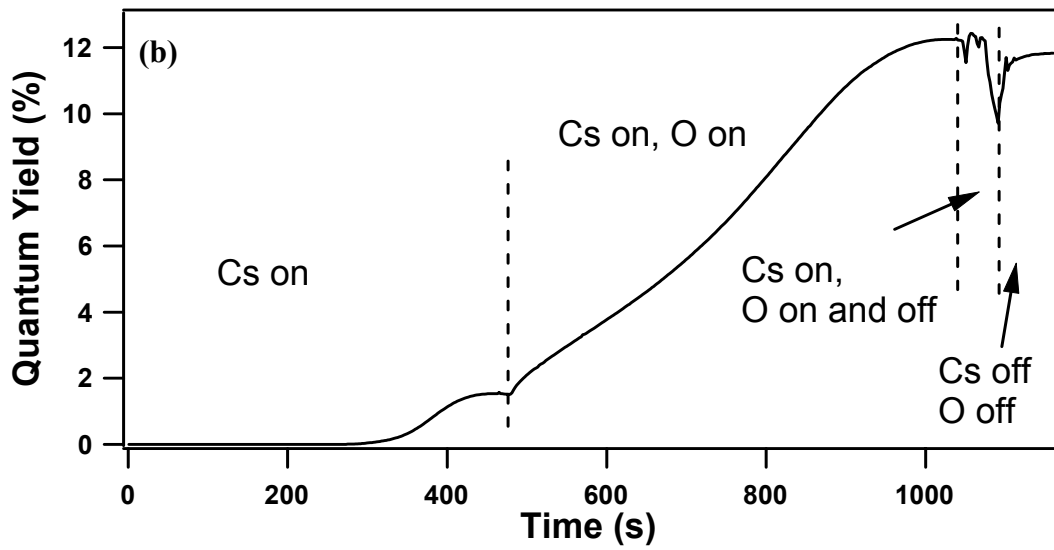
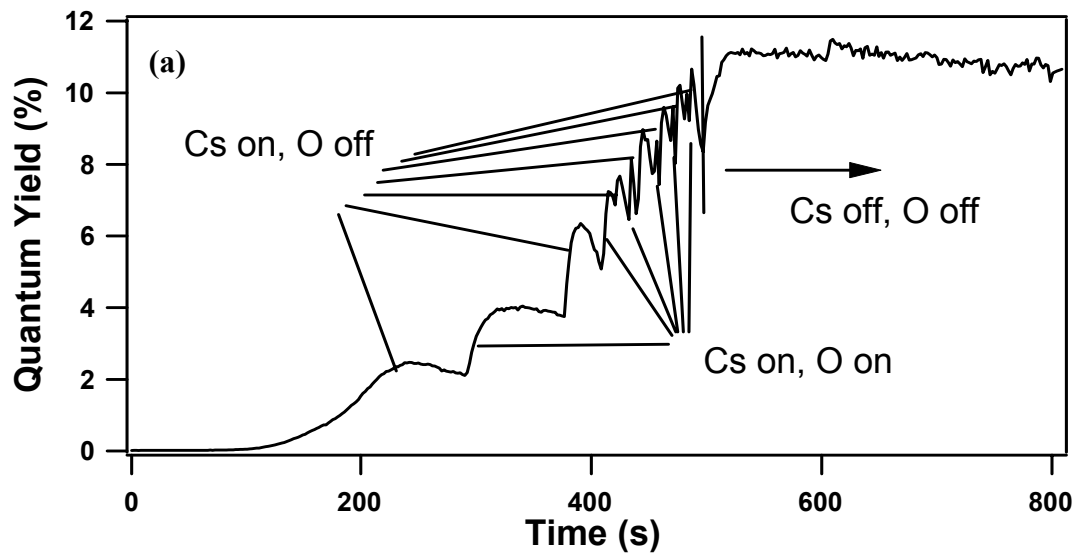


Figure 1

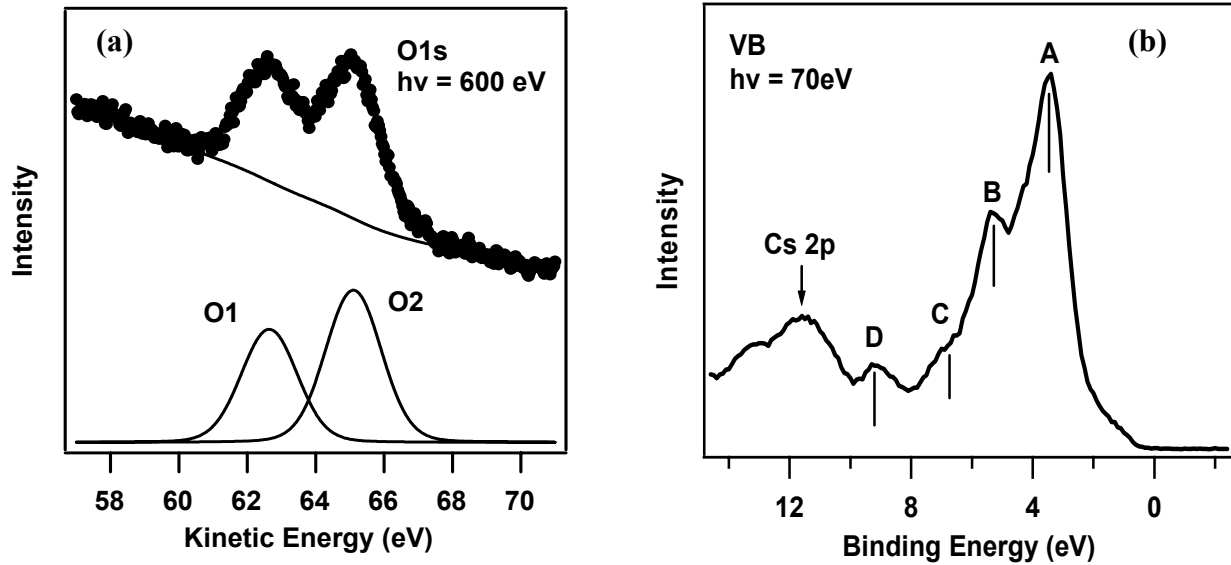


Figure 2

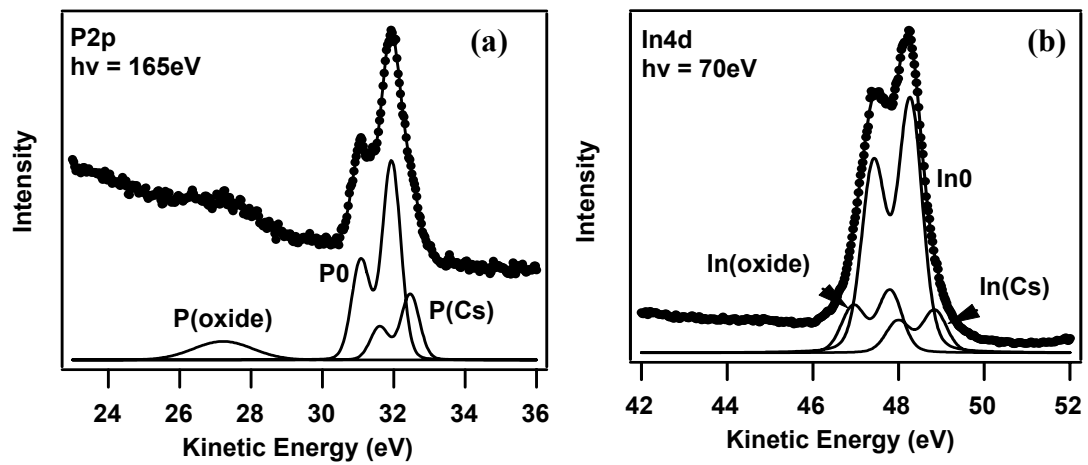


Figure 3

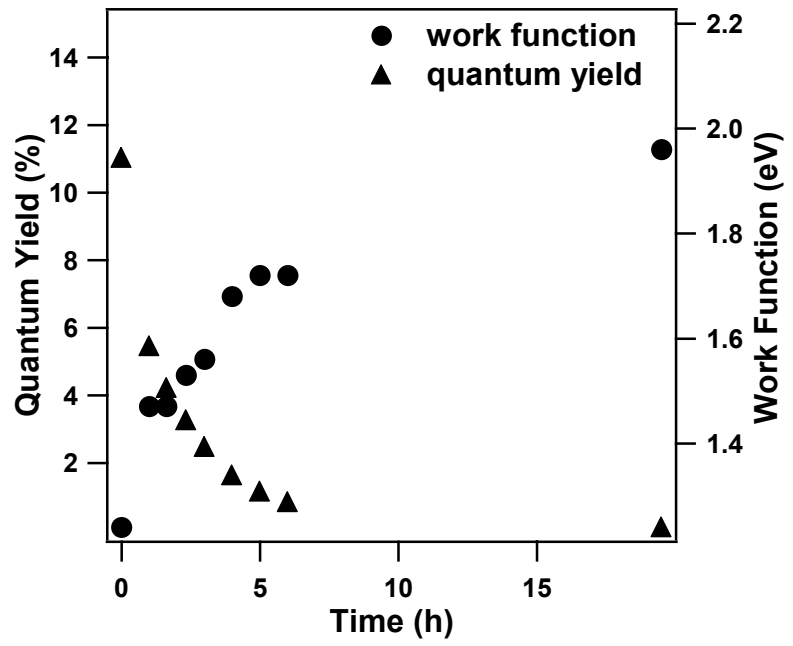


Figure 4

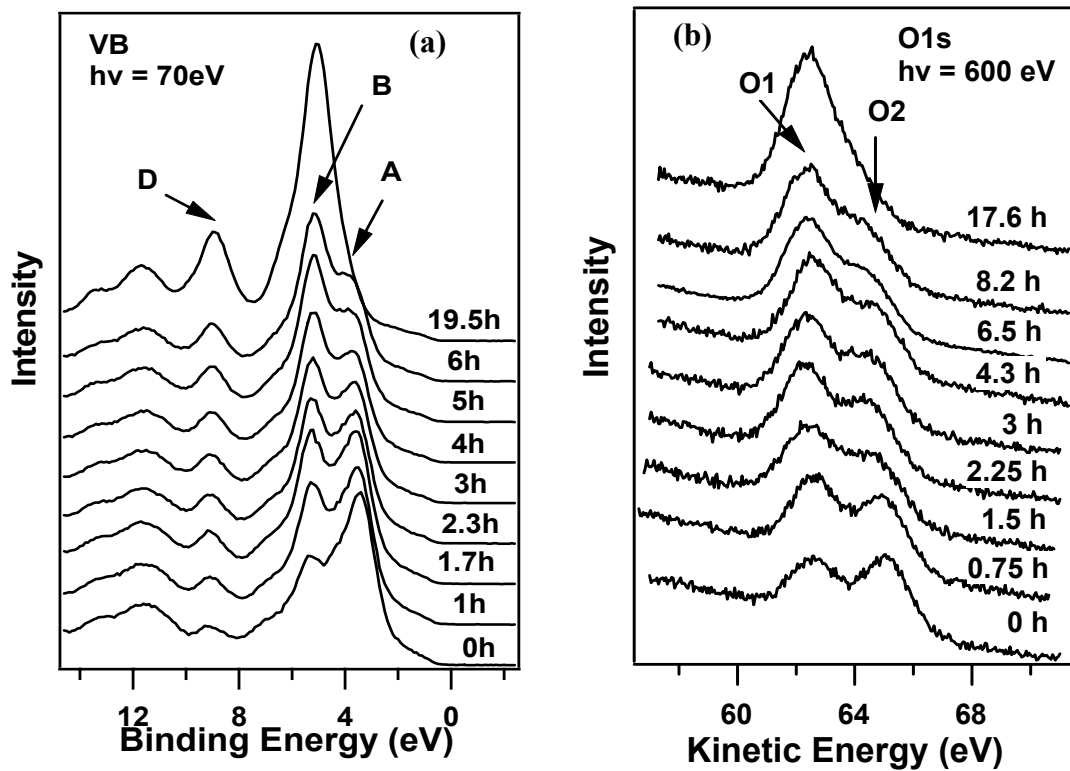


Figure 5

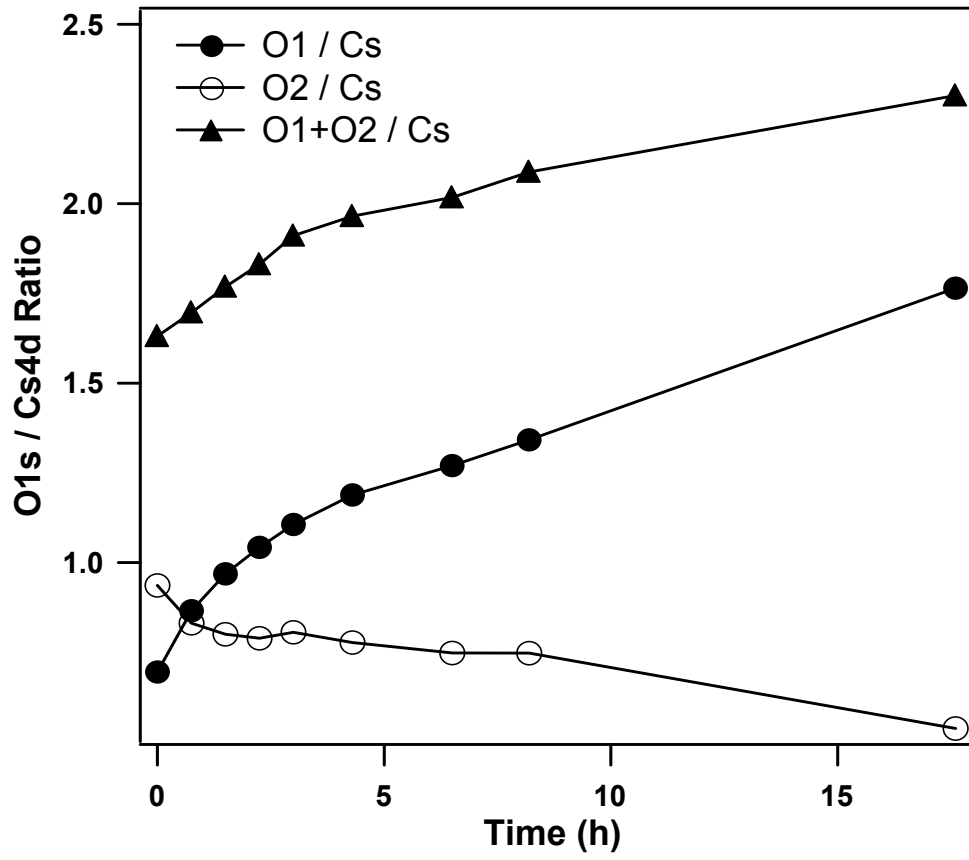


Figure 6

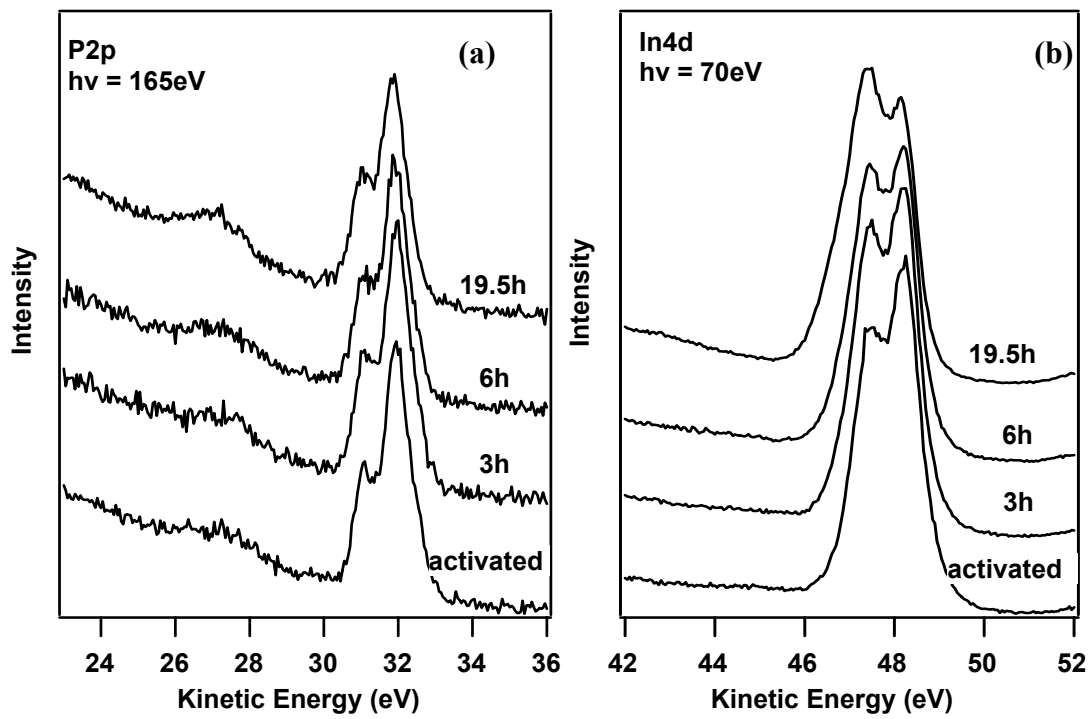


Figure 7

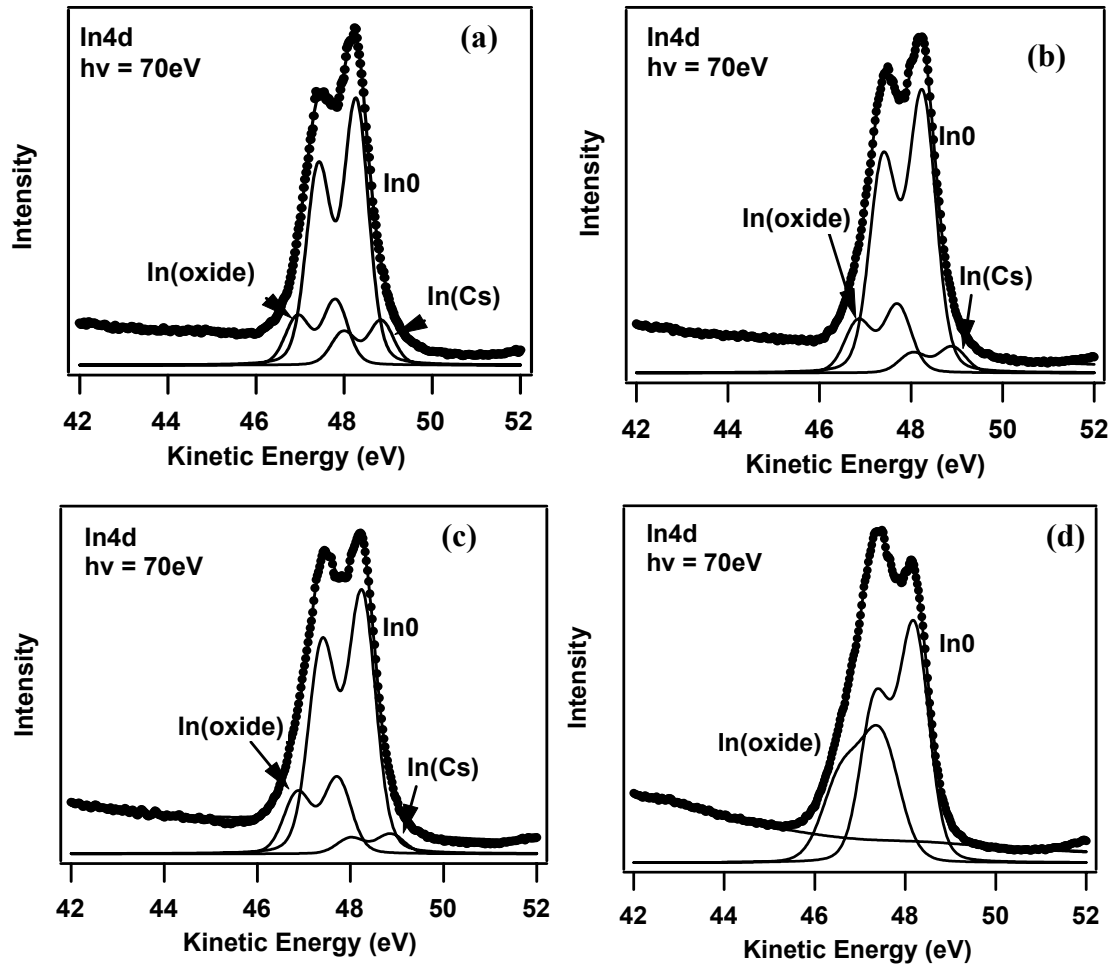


Figure 8

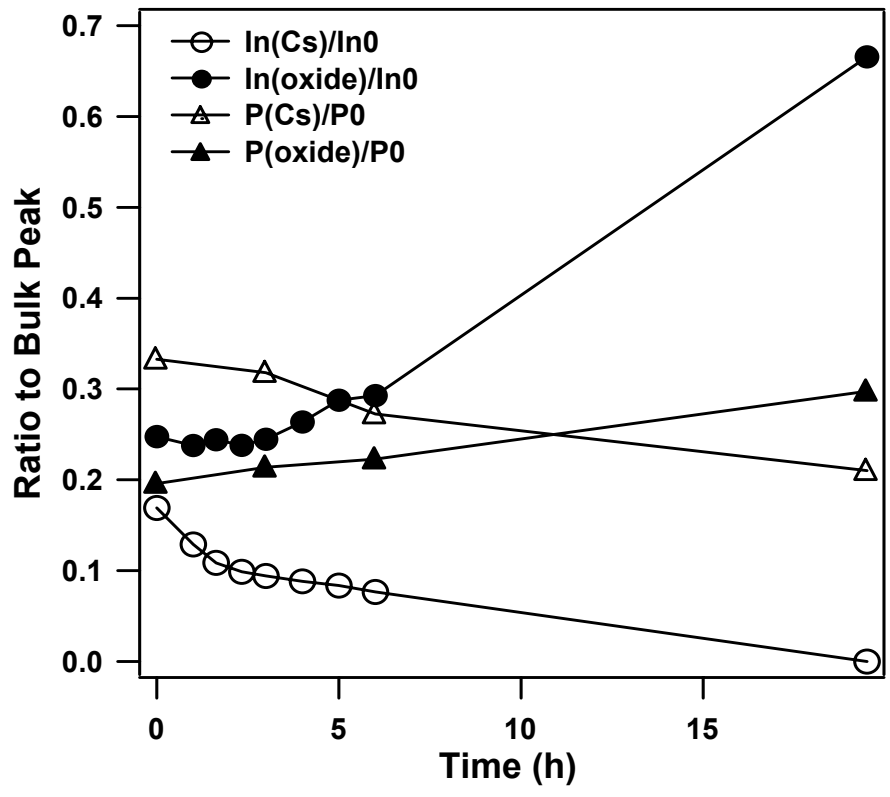


Figure 9