# Effects of thinning and heating for $TiO_2$/AlInP junctions

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**Abstract**

$TiO_2$/AlInP junctions are used to construct the antireflection coatings for solar cells and to passivate III-V nanostructure surfaces. The thickness of AlInP epilayer affects light absorption and appropriate Al composition determining further the energy barrier for carriers. We report on reducing the AlInP thickness by dry etching down to 10 nm without introducing harmful defect states at $TiO_2$/AlInP interface and AlInP/GaInP interface below, according to photoluminescence. Synchrotron-radiation photoelectron spectroscopy reveals that increased oxidation of phosphorus is not harmful to $TiO_2$/AlInP and that post heating of the material enhances AlInP oxidation and group III element segregation resulting in decreased material homogeneity.

*Keywords:* AlInP, $TiO_2$, passivation, solar cell

## 1. Introduction

The epitaxial $Al_{1-x}In_xP$ film with a large energy band gap is widely used as a standard window layer of high-efficiency III-V multijunction solar cells and also as a protective cap of III-V nanostructures, to prevent the surface/interface recombination of electric carriers[1, 2]. Such semiconductor nanocrystals are investigated for various applications in the fields of electronics, optoelectronics, sensor technology, and water oxidation (hydrogen production) technology for instance. Understanding and processing physical properties of the interfaces of nanoscale semiconductor films and crystals are relevant to develop the applications because the surfaces form a very essential part of the whole materials. Often the AlInP film is still covered by oxide films, for example, by an antireflection (AR) coating stack of $SiO_2/TiO_2$ or $Al_2O_3/TiO_2$. The target is to keep the high-quality epitaxial AlInP/III-V interface with a low density of electronic states around the band gap. This is complicated by the fact that the surface of the AlInP layer becomes easily oxidized and amorphous if in a contact of oxygen-containing environment. Thus, the AlInP film should be thick enough to avoid the oxidation of the whole AlInP layer, which could deteriorate the crucial epitaxial AlInP/III-V interface. On the other hand, the absorption increases with increasing thickness of the AlInP layer and

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thus the efficiency of the solar cell decreases. Furthermore, the Al composition needs to be optimized for appropriate band gap and energy barriers, which in turn affects the critical thickness of AlInP without structural relaxation and defect formation. The composition of $Al_{1-x}In_xP$ with $x \approx 0.5$ was used in this study. This structure is lattice-matched for GaAs(100) and results in an indirect band gap of 2.3 eV[3]. The effects of thinning and processing of AlInP layer are also important in applications where nanopatterning on the outer layers of solar cells are utilized. These include e.g. moth-eye type anti-reflection patterns [4].

It is challenging, in general, to investigate the buried and thin interface layers. Moreover the oxide/III-V interfaces are often amorphous making the atomic-scale studies difficult. The combination of photoluminescence (PL) and core-level photoelectron spectroscopy (PES) characterizations has been previously shown to be an efficient approach to elucidate these interface issues[5–8]. The PL intensity is sensitive to the interface defect density while the core-level spectra of the interface elements, measured through a thin oxide film (2-4 nm), provide information about the atomic structure of the buried interface. Here, by utilizing these methods with state-of-the-art synchrotron-radiation (SR) facilities, we report that it is possible to reduce the AlInP thickness to 10 nm by dry etching before $TiO_2$ deposition, and to control the surface oxidation such that the epitaxial structure and electrical quality of the $TiO_2$/AlInP/GaInP heterostructure remain. The results also elucidate the composition of $TiO_2$/AlInP interface and, in particular, answer the questions how the heating affects the heterostructure and why.

## 2. Experimental

Total of six samples were prepared. Each of them contained a GaInP solar cell with AlInP window layer and GaAs contact layer grown on p-GaAs(100) substrate with molecular beam epitaxy (MBE). For all the samples the topmost n-GaAs epilayer was selectively etched by immersion in 1:30 $H_2O_2$:$NH_4OH$ -solution. Subsequent dry etching treatment for three samples was done with commercial inductively coupled plasma reactive ion etching (ICP-RIE) system. An etchant gas mixture of $Cl_2$/$N_2$/Ar 10sccm/15sccm/2sccm with an initial strike pressure in the chamber of 7 mTorr with gradual ramp to a chamber pressure of 3 mTorr was used to establish a stable plasma. Source ICP power was 500 W and RIE chuck power was set to 50 W. The sample plate temperature was set to 200 °C.

For the 50 nm thick AlInP-layer, etching parameters were adjusted from the previous moth-eye etching[4] to slow down the etching process for enhanced controllability. A short etching treatment of 10 s resulted in an etch depth of 35-40 nm measured with profilometer, which resulted in a 10-15 nm thick epitaxial AlInP layer on GaInP. After ICP-RIE, all the samples except two reference samples with and without ICP etching were loaded into an electron-beam dielectric coater. A 3 nm $TiO_2$ film was deposited on these samples. Air exposure time between dry etching and dielectric coating was 90 min. In addition, high temperature RTA treatment was done at 750 °C for 60 s for one $TiO_2$ coated, dry etched sample and one $TiO_2$ coated, non-etched sample. The purpose was to maximize or discern heating effects possibly occurring during device fabrication and over time. The treatments are recapitulated in table 1. Room-temperature PL spectra were measured using an Accent RPM2000 PL mapping tool equipped with a frequency

Table 1: The treatments carried out for each sample. '$H_2O_2$:$NH_4OH$' refers to the selective wet etching of contact-GaAs layer and 'ICP' to the dry etching of AlInP layer.

| Sample | $H_2O_2$:$NH_4OH$ | ICP | $TiO_2$ | RTA |
|---|---|---|---|---|
| 1 | x | x | x | x |
| 2 | x | x | x | |
| 3 | x | x | | |
| 4 | x | | x | x |
| 5 | x | | x | |
| 6 | x | | | |

doubled 532 nm Nd:YAG laser and a GaInAs detector array. High-resolution SR-PES was performed at the MAX-lab on beamline I311.

### 3. Results and discussion

Changes in the PL intensity of GaInP between the samples described above are influenced by the AlInP/GaInP interface and the AlInP surface or interface with $TiO_2$: higher intensity indicates better quality of the interfaces. For the RTA treated samples, also the effects in bulk should be considered. The PL spectra in figure 1 show a slight improvement of the intensity for the dry etched samples as compared to the samples without the AlInP thinning. This small difference can be also due to changes in the bulk GaInP quality over the two-inch wafer grown, from which the samples were cut, as exemplified in the top PL map of the insert. However, the PL results reveal that the harmful surface/interface recombination does not increase due to the AlInP thinning and the $TiO_2$ growth. This indicates that the epitaxial AlInP/GaInP interface is preserved also in the thinned samples and that the quality of the $TiO_2$/AlInP interfaces is similar to the air-oxidized AlInP surface, as characterized by the PL measurements. Also, the absorption of the incident light in the indirect band gap window layer is quite insignificant and unaffected by the different treatments.

In contrast, the post heating causes significant inhomogeneity in the PL signal over the sample (the bottom image of the insert of figure 1), in addition to about 5 nm shift in the peak wavelength. The peak intensity over the sample is lower in the center but notably higher on the edges. It is important to note that identical behavior after RTA treatment was observed for the etched sample implying that for the observed effects higher thickness of the window layer plays no significant role during heating.

To elucidate mechanisms behind the above changes, SR-PES measurements were carried out with a variety of photon energies (500-1300 eV) to probe the core levels of the elements at the buried $TiO_2$/AlInP interfaces and also below the interfaces with high enough photoelectron kinetic energies. Figures 2 and 3 present Ga $2p_{3/2}$, In $3d_{5/2}$, P 2p, and Al 2p spectra with fittings for selected samples. Clear heating-induced spectral changes can be observed,

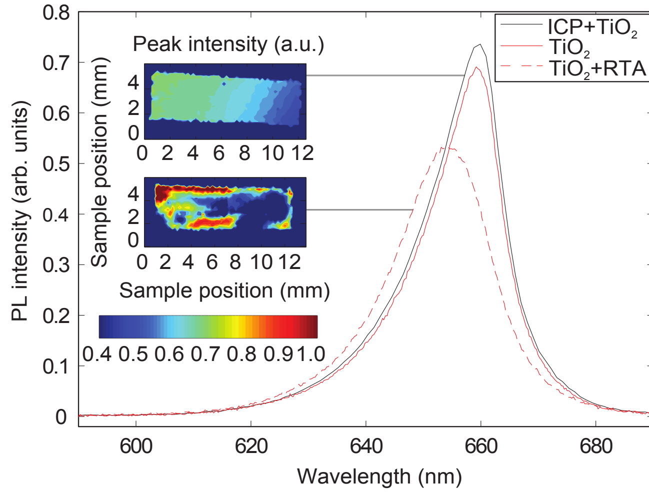


Figure 1: PL-spectra of samples with different treatments and PL peak intensity maps of a sample before and after RTA. The variation of PL-intensity on the sample edge of upper inset is due to very close proximity to the wafer edge from which the samples were cut. PL-spectra were measured from the center of the samples.

in consistency with the PL results. First, a very surface-sensitive Ga $2p_{3/2}$ emission appears (figure 2) after the RTA, indicating the segregation of Ga atoms from GaInP toward the surface. This can be understood via drastic structural transformations at the $TiO_2$/AlInP interface and concomitant Ga diffusion, most likely, along possible grain boundaries. The initial diffusion of Ga is, however, likely caused by group III vacancies at the $TiO_2$/AlInP interface that are diffused towards GaInP and result in changes in ordering of the structure. The presence of this of mechanism is also observable systematically in Fig. 4, in which the emission intensity of In $3d_{5/2}$ is compared with the adjacent Ti $2p_{3/2}$ peak. The surface sensitivity of lower energy photon measurements indicate that In also permeates in the $TiO_2$ layer due annealing as it is observed more prominent on the surface. Note that the relative cross-sections of these photoemission peaks do not significantly vary with the photon energies used here ($\sigma_{\mathrm{In3d}}/\sigma_{\mathrm{Ti2p}} \approx 2.4-2.9$)[9]. Thus, some site exchange of In and Ga can also be expected. These suggestions agree with the observed shift in the PL intensity and peak wavelength.

Furthermore, the elements of AlInP become almost fully oxidized during the RTA because their core-level spectra include mainly broad oxidation-induced peaks on the high binding-energy side of the sharper peaks that arise from the pure semiconductor crystal (figures 2 and 3). Almost total disappearance of the pure semiconductor peaks indicates that the thickness of the oxidized surface part increases by at least about 2 nm during RTA, as the information depth of PES contains only oxidized species. Considering the studied $TiO_2$/AlInP junction one can expect, in particular, an enhanced oxidation of Al due to its exothermic nature. The 2p transition peak of oxidized Al is observed to shift to a lower binding energy after RTA, corresponding to more stable oxides [10] such as $\alpha$-$Al_2O_3$ indicating significant structural changes in the interface. Also, some non-stoichiometric amorphous Ti-Al-O phase can cause such a broad and shifted peak. Thus, we suggest that the RTA-induced structural changes are promoted by the formation of Al-

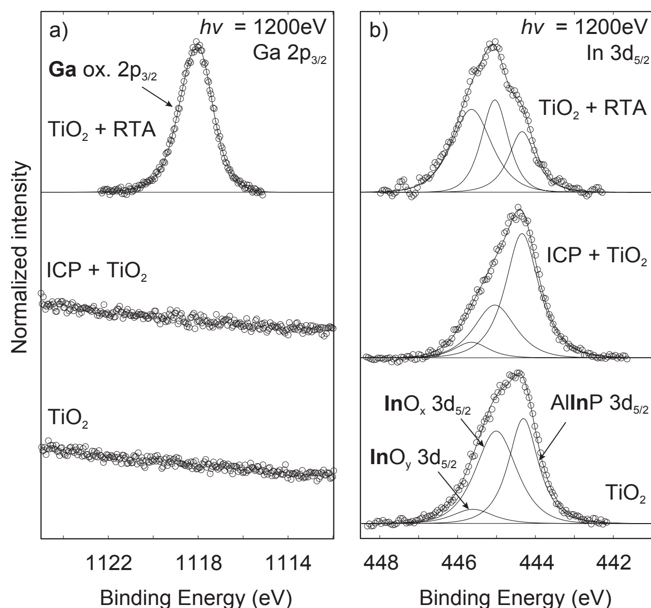


Figure 2: PES-spectra for a) Ga $2p_{3/2}$ and b) In $3d_{5/2}$ transitions. In the In $3d_{5/2}$ spectrum, a higher binding energy peak is observed after RTA, corresponding to a higher oxidation state.

oxide phases, which are thermodynamically more stable than Ti-oxides [11], at the interface. Rearrangement in Al-bonding will also relieve In and thus assist in the permeation discussed above. From Fig. 4 it can be seen that the initial Ti-oxide composition is not purely $TiO_2$ but also some lower oxidation states of Ti exist in the structure. After annealing, however, practically only $TiO_2$ or, more generally, $Ti^{4+}$ species exist, especially near the AlInP interface. This result is consistent with the conclusion that new oxide phases begin to form at the interface, where TiO and intermediate $Ti_xO_y$ species act as initiate building blocks. Here the elevated RTA temperature has been used in order to speed up oxidation and distinguish the differences, but transformations may also occur at lower temperatures of the concentrated photovoltaic cells and in a longer time scale, leading to gradual degradation of these components.

Initial composition of AlInP near $TiO_2$ interface due to the $H_2O_2$:$NH_4OH$ treatment (residual effects of GaAs etching) and subsequent oxidation in the air can be observed in the lowest spectra of figures 2 and 3. For each element, the oxidation with respect to the non-oxidized state is quite similar. Concerning the changes in the spectra of the samples with and without ICP etch, it can be seen in figures 2 and 3 that at the AlInP surface of the former sample, aluminum and phosphorus are more oxidized than at the latter sample surface: the ratio of high binding-energy emission to the pure semiconductor emission is higher for the dry etched samples. Interestingly, the amount of In surface oxides is, vice versa, lower for the dry etched sample. Previously the effects of different III-V surface oxides on the formation of electron states at the oxide-semiconductor interfaces have been intensively studied[12–15]. Since the $TiO_2$/AlInP interface quality does not change significantly with the dry etching, according to the PL results in figure 1, there are the following possible scenarios: If the formed In oxide phase is harmful, the Al oxide and/or P oxide improve the interface quality. If the In oxide does not affect the defect state density, (i) either the Al and P oxides

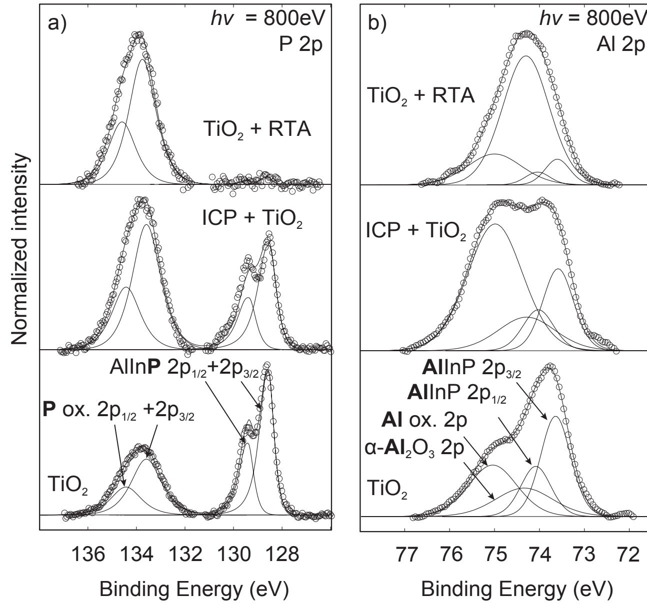


Figure 3: PES-spectra for a) P 2p and b) Al 2p transitions with peak splitting observed for lower binding energy states, attributed to AlInP bonding, and envelope spectra for higher binding energy oxidized states with visible peak splitting only for P 2p.

do not affect or (ii) the effects of Al and P oxides are opposite. Even if the AlInP/GaInP interface decreases movement of the PL-induced carriers to the $TiO_2$/AlInP interface, the passivation is usually not perfect and $TiO_2$/AlInP interface effects need to be considered.

The PL results showed that the AlInP window layer still retained its epitaxial interface structure with GaInP after the dry etch process and the $TiO_2$ deposition. This is clearly supported by the core-level spectra showing the presence of the emissions from the pure AlInP crystal together with the emissions from the oxidized surface parts of AlInP. Therefore, the AlInP film is not fully oxidized.

## 4. Conclusions

In conclusion, it has been demonstrated that the ICP-RIE dry etching can be utilized to thin the AlInP window layer down to 10 nm, e.g. for high-efficiency solar cells, keeping still the epitaxial structure of AlInP/GaInP and quality of the $TiO_2$/AlInP/GaInP heterostructure without increasing the harmful surface and interface recombination. However, the core-level spectra reveal changes due to the etching: the amount of In oxides decreases while the Al and P oxidations increase. The post heating is found to cause significant inhomogeneity in the PL intensity. The spectra elucidate the mechanisms behind the changes and reveal clear structural transformations, in particular, the strong group III element segregation which are suggested to be promoted by the energetically favored formation of Al oxides at the junction. The presented synchrotron-radiation based approach is expected to be useful to elucidate the buried properties of various semiconductor interfaces.

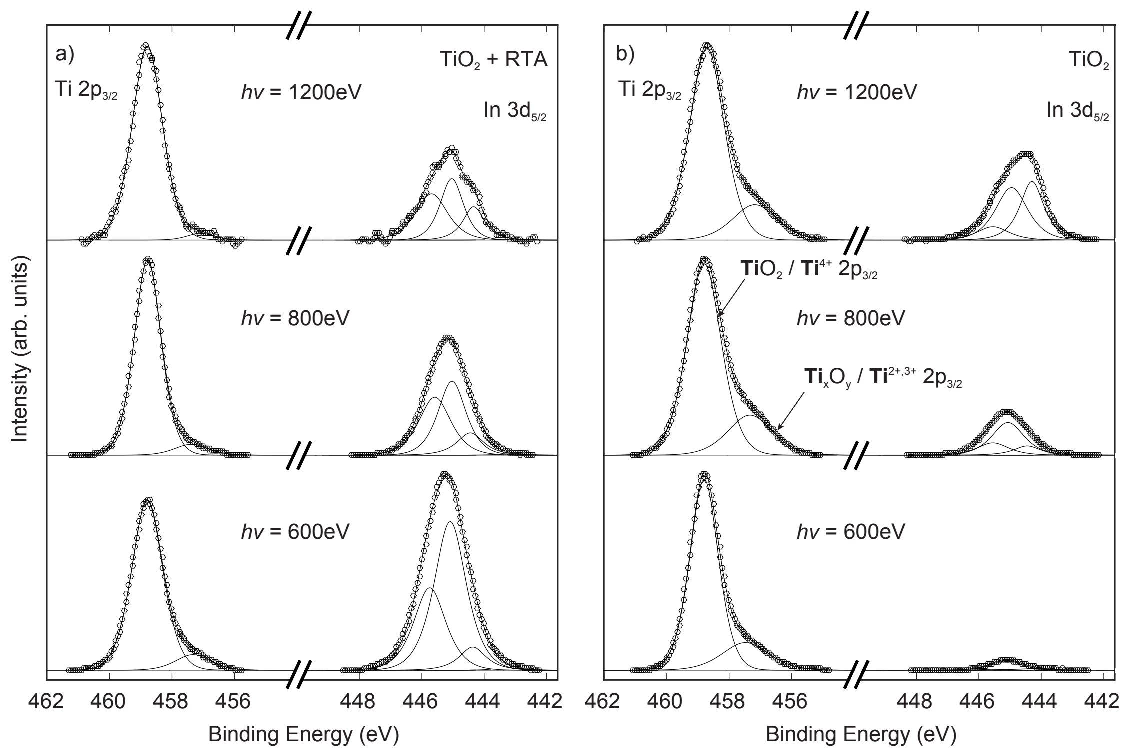


Figure 4: PES-spectra with various photon energies for Ti $2p_{3/2}$ and In $3d_{5/2}$ for samples with a) $TiO_2$ coating and subsequent RTA treatment and b) only $TiO_2$ coating for reference. The heating induces movement of In towards the surface: the more surface sensitive measurements give higher intensity for In 3d compared to Ti 2p, as opposite to the expected lower intensity with higher surface sensitivity for the reference sample. Similarly, the decrease in the lower oxidation states of Ti is observed especially near the buried interface.

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