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Preparation and characterization of GaP semiconductor electrodes for photoelectrochemical water splitting

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Abstract

p-type GaP was systematically examined for photoelectrochemical water splitting. The influence of wet chemical etching and the difference of electrochemical deposition and physical vapor deposition of platinum were investigated. Therefore, each preparation step of GaP was studied by photoelectron emission spectroscopy, atomic force microscopy and photoelectrochemical methods.

Keywords:

gallium phosphide, water splitting, hydrogen, platinum, electrochemistry, photoemission

1. Introduction

Gallium phosphide is a semiconductor with a band gap of about 2.3 eV [1]. The wide band gap theoretically provides enough energy to split water directly in a photoelectrochemical cell (PEC). Therefore GaP has already been intensively studied for PEC-applications ([2], [3], [4]). Additionally it is a promising electrode because of its stability in electrolytes under cathodic conditions. This is caused by the slow kinetics of the cathodic dissociation reaction of GaP and by the rapid formation of a thin oxide layer in electrolytes [5]. Still, it does not show the expected photoelectrochemical behavior. The photocurrent onset of hydrogen evolution is nearby 0 V vs NHE despite the wide band gap of GaP. In order to improve the kinetics of the hydrogen evolution Nakato et. al. deposited platinum particles on top of GaP which results in an increased efficiency of the PEC [6]. Contrary to that, Goodenough et. al. observed that different metals can influence the PEC behavior, but especially platinum on GaP has a negative effect for the hydrogen evolution [7]. So, it is still not clear today on how to improve a GaP electrode to get the desired efficiency in a PEC.

The interface region between the semiconductor and the electrolyte primarily determines the properties of a PEC. The focus of this work is to achieve a basic understanding of the influence of the interface structure on the efficiency of a p-GaP PEC in order to improve its performance drastically. Therefore a chemical analysis of the interface region of GaP is performed by photoemission spectroscopy for each preparation step. First, the surface is chemically etched to remove the native oxide layer. Second, platinum islands are deposited by electrochemical deposition or by physical

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vapor deposition. Furthermore, the samples are characterized electrochemically and by atomic force microscopy after each step.

2. Experimental procedure

Gallium phosphide samples were p-type with a doping level of $1.1 \cdot 10^{18} \text{ cm}^{-3}$. They were cut out of a single crystalline wafer with an orientation in (100) direction. The wet chemical treatment was done in a glass chamber which was filled with argon. This chamber was directly connected to the “Solid Liquid Interface Analysis System” (SoLiAS) at BESSY [8]. There the samples were etched with concentrated hydrochloric acid. Platinum was deposited electrochemically out of a solution of potassium tetrachloroplatinate (0.5 mM) in perchloric acid (1 M). The deposition current was kept at about $20 \mu\text{A} \cdot \text{cm}^{-2}$ for 100 s. The deposited amount of platinum corresponds to 2.2 monolayer. On an additional sample, which was etched like mentioned above, platinum was deposited by physical vapor deposition in a nearby chamber without breaking vacuum.

The photoemission spectra of the samples were measured without exposure to air. Monochromatic synchrotron light of the BESSY II storage ring with an energy of 120 eV was used as light source. After that the samples were removed from the UHV system and the topography of the samples was measured by a non-contact atomic force microscope (MFP-3D from Asylum Research). For electrochemical characterization a “Controlled Intensity Modulated Photo Spectroscopy” setup (ZAHNER-Elektrik GmbH & Co.KG) was used. The electrochemical measurements were done in 0.1 M hydrochloric acid with a silver/silver chloride reference electrode in 3 M NaCl (0.209 V vs NHE). A white light LED with an intensity of $100 \text{ W} \cdot \text{m}^{-2}$ was used for the standard measurements. For quantum efficiency measurements monochromatic LEDs with wavelengths from 431 to 979 nm were used. Their intensity was measured with the supplied photodiode. All chemicals used were reagent grade.

3. Results and Discussion

3.1. Photoemission

The photoemission spectrum of the untreated sample (figure 1.Ia) shows three emission lines in the Ga3d region. The line at 19.4 eV can be attributed to pure GaP. The second line at 20.9 eV stems from gallium oxide. The oxide film usually consists of different types of gallium oxides, which will not be regarded separately in this investigation. The flat peak at 24.4 eV can be attributed to the O2s emission line. The spectrum of the untreated sample displays a strong drop of the valence band at 3.4 eV (figure 1.Ib) and a long tail up to 0.7 eV. This behavior is in accordance with reference data for Ga_2O_3 [9].

Figure 1.IIa displays the spectrum after etching in concentrated hydrochloric acid. The GaOx emission line vanishes almost completely and the O2s line is not visible anymore. But there is still an additional peak at the high energy side of the Ga3d emission line of GaP. The existence of this broad peak is a clear signature, that there is a small amount of oxide left on the surface. The valence band shows a prominent peak at a binding energy of 3.5 eV, which can be attributed to the clean GaP. The valence band edge (figure 1.IIb) is at 0.7 eV binding energy, which is too high with respect to a highly doped p-type semiconductor. But the energetic difference between the edge and the Ga3d core line is in good agreement to an expected photoemission of a clean GaP surface [10]. This observation can be explained by a band bending at the GaP interface. Because the Ga3d line is not shifted due to the etching step, it can be assumed that the band bending already exists before etching.

After the electrochemical platinum deposition the Ga_xO_y emission line (figure 1.IIIa) is shifted slightly to higher binding energies. This indicates that a weak reoxidation of the surface occurs. The GaP emission line is not affected by the platinum deposition. Furthermore figure 1.IIIb shows no shift of the valence band edge, but a change in the electronic structure below the edge is clearly visible. The 4f doublet of platinum (figure 1.IIIc) is located at 72.4 eV, and 75.7 eV. With respect to reference data the Pt4f lines should be found at 71.2 eV, and 74.5 eV for the bulk material [11]. This deviation indicates that there is still some amount of unreduced platinum chloride left on the surface.

The deposition of platinum via PVD has a different effect on the photoemission from etched GaP. The Ga3d line in figure 1.IVa is shifted by 0.3 eV to lower binding energies and its width increases. After the deposition the valence band edge shows a tail, which extends above 0 eV binding energy (figure 1.IVb). The Pt4f lines are at 72.0 respectively 75.3 eV. This small difference to bulk values can be explained by the different screening effects in small size platinum islands [12].

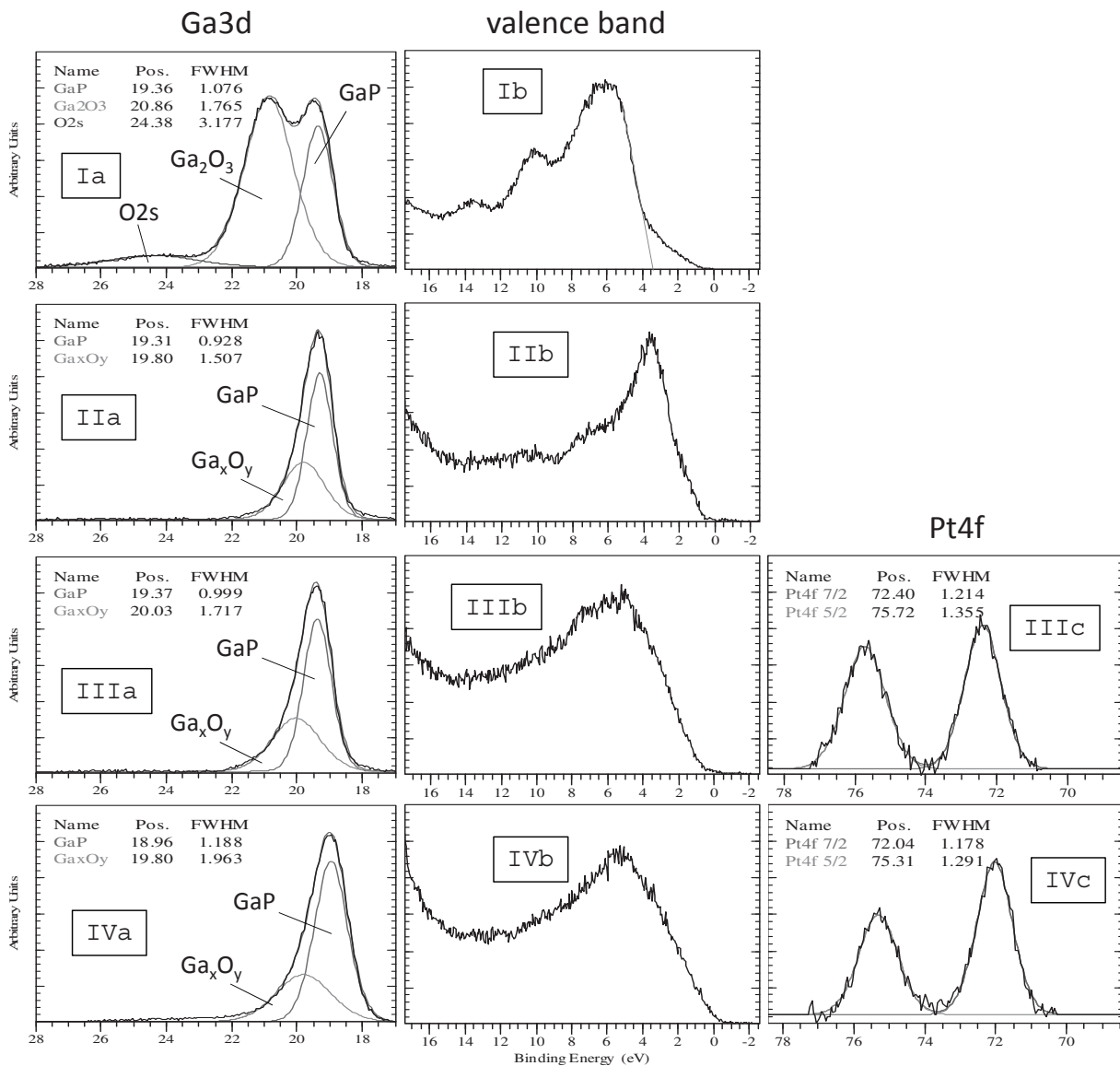


Figure 1: Photoemission spectra of p-type GaP after different preparation steps. Excitation energy was 120 eV. From top to bottom: untreated sample (I), sample after etching in hydrochloric acid (II), etched sample after electrochemical deposition of platinum (III), etched sample after platinum coating by PVD (IV). For more information see the discussion in the text.

3.2. Topography

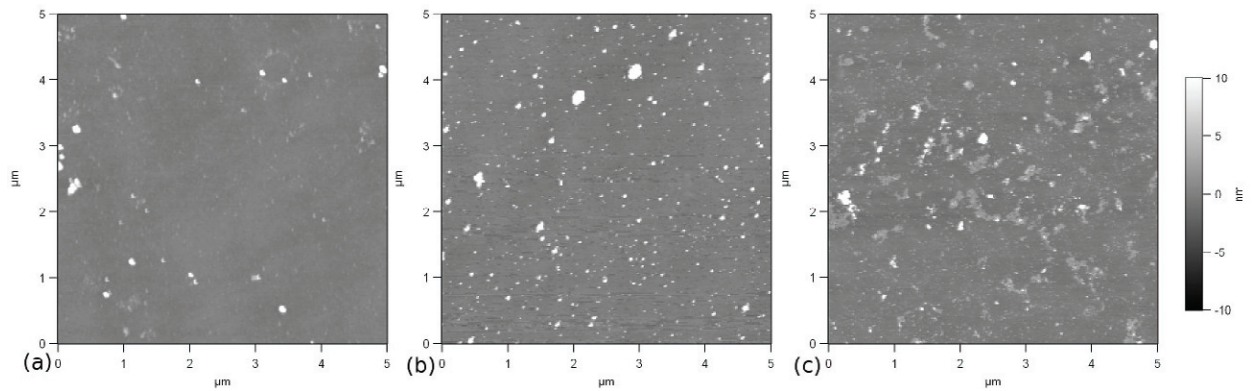


Figure 2: Atomic force micrographs of p-type GaP: (a) etched in hydrochloric acid and (b) electrochemical deposition of platinum and (c) platinum coating by PVD

Figure 2(a) shows the topography of the etched GaP. The etchant leaves some particles with a diameter of about 40 nm on the surface. It is possible that the particles stem from a reoxidation process while the etching has taken place or after exposure to air. After the electrochemical deposition of platinum the amount of particles has increased (figure 2(b)). It is not clear at the moment, if all the additional particles observed by AFM are indeed platinum or if they are due to an oxidation process during the platinum deposition. The particles have diameters from 50 to 150 nm and their height is about 20 nm. The second deposition method using a electron beam evaporator results in a 2D-island growth, as shown in figure 2(c). The evaporated platinum accumulates in terraces with a height of 1.5 nm. These terraces cover about 10 % of the semiconductor surface which leads to a total amount of 0.8 monolayer of platinum.

3.3. Electrochemical characterization

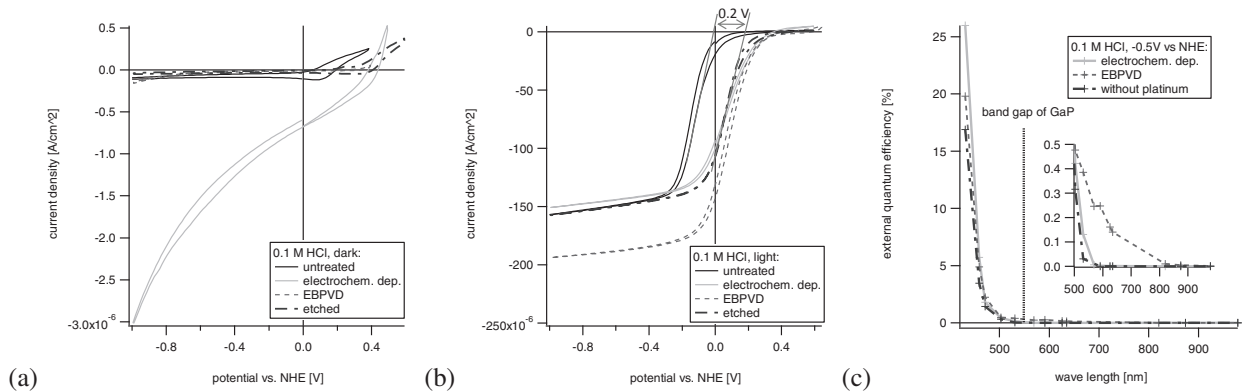


Figure 3: Current-Voltage curves of p-type GaP in 0.1 M HCl (a) in the dark and (b) under illumination by white light LED ($100 W \cdot m^{-2}$). (c) Quantum efficiency in 0.1 M HCl at -0.5 V vs NHE. The quantum efficiency is not corrected for absorption or reflection.

Figure 3(a) shows the dark current characteristics after the different preparation steps. The cathodic current is low as expected for semiconductor electrodes except for the sample with the electrochemically deposited platinum. The higher current points to an additional reduction of unreduced platinum on the surface. This supports the explanation done by photoemission spectroscopy in figure 1.IIIc.

The electrochemical behavior under illumination is displayed in figure 3(b). Untreated GaP shows a photocurrent onset at 0 V vs NHE. After the etching in concentrated hydrochloric acid the onset of the photocurrent shifts 0.2 V in anodic direction. Electrochemical deposition of platinum leads neither to a further shift of the photocurrent onset

nor to an increase in current. Contrary to this the platinum deposited by PVD increases the photocurrent by 25%. The photocurrent onset is shifted only slightly to anodic direction.

The external quantum efficiency of the treated GaP samples in figure 3(c) can be separated in two regions. For photon energies above the band gap of gallium phosphide the external quantum efficiency of the platinum deposited samples are very similar to etched GaP without platinum. At 431 nm it reaches 20 %, which is in good agreement with literature data [13]. In contrast to the previous samples, the sample with platinum deposited by PVD shows an additional response in the sub-band gap region. This behavior is not unusual for gallium phosphide. It is assumed, that additional energy levels “metal-induced-gap-states” are the reason [14].

4. Summary and Conclusion

In this work the influence of different treatments of p-GaP was systemically studied by photoemission spectroscopy, atomic force microscopy and electrochemical methods.

The etching with concentrated hydrochloric acid removes the native gallium oxide layer almost completely and only a thin oxide layer remains at the GaP surface. The onset for photoelectrochemical water splitting is shifted by 200 mV to the anodic direction. The so prepared surface shows reproducible results even after prolonged (one month) exposure to atmospheric conditions.

The electrochemical deposition does not result in a shift of the Ga3d emission line, which would be expected if there is a Schottky barrier formation between GaP and platinum. There is also no sub-band gap response observable in the quantum efficiency which would indicate a direct contact of platinum particles to GaP. So we conclude, that electrochemical deposition generates platinum particles actually on top of the remaining oxide layer. The reduction of $PtCl_4^{2-}$ is not fully accomplished during the deposition, which is supported by the electrochemistry and the photoemission spectroscopy data. This could explain the absence of an increased efficiency of the PEC after electrochemical platinum deposition.

PVD of platinum shifts the valence band edge and changes the form and position of the Ga3d line. It causes a sub-band gap response in the quantum efficiency which gives evidence to a direct platinum-semiconductor contact. Also, the shift of the Ga3d line can be explained by a Schottky barrier formation. But a change in the photocurrent onset due to the lower band bending is not visible in the current-voltage curve. Therefore a precise analysis of the formed Pt-GaP contact is necessary to fully understand the properties of such a device.

Atomic force microscopy data show a clear difference in the growth behavior between electrochemical deposition of platinum (3D) and PVD (2D). To get further information from this type of investigation a thoroughly cleaned and well defined GaP surface will be necessary.

Future experiments will have to start from a well defined, atomically clean surface. The formation of the oxide buffer layer has to be controlled precisely. The effect of platinum particle size and island form and density on the electronic structure and on the PEC behavior will have to be studied in more detail.

5. Acknowledgment

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