Eur. Phys. J. D **24**, 373–376 (2003)
DOI: 10.1140/epjd/e2003-00162-1

THE EUROPEAN
PHYSICAL JOURNAL D

Photoemission study of size selected InP nanocrystals: the relationship between luminescence yield and surface structure

S. Adam[1,a], C. McGinley[1], T. Möller[1], D.V. Talapin[2], H. Borchert[2], M. Haase[2], and H. Weller[2]

[1] HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany
[2] Institute of Physical Chemistry, University of Hamburg, Bundesstr. 45, 20146 Hamburg, Germany

Received 10 September 2002

Abstract. The surfaces of luminescent InP nanocrystals were investigated by photoelectron spectroscopy (PES) technique with synchrotron radiation. Semiconductor samples were prepared by an organometallic approach using trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) as stabilizing and size regulating agents. As prepared, InP nanocrystals exhibit poor photoluminescence (PL) yield, usually less than 1%. However the yield can be drastically enhanced to about 20−30% by photoetching of the nanoparticle surface with fluorine compounds. High resolution In 3*d* and P 2*p* core level spectra of etched and non-etched particles taken at different excitation energy reveal changes of the nanocrystal surface. Three different InP samples are analyzed and a simple model for the etching process is discussed.

PACS. 79.60.Jv Interfaces; heterostructures; nanostructures – 78.55.Cr III-V semiconductors

1 Introduction

Colloidally prepared semiconductor nanocrystals show a very successful way of producing new materials with size dependent electronic and optical properties [1]. Modification of the surface can dramatically increase nanocrystal luminescence, which combined with the band-gap size dependencies leading to new technologies such as nanocrystal optical displays, lasers and biological labeling. Surface passivation with ligand chains is essential for the stability of such II-VI and III-V systems. It would be useful to clarify the chemical nature of the surface states in order to improve the photoluminescence yield for further nanostructure applications.

While II-VI semiconductor nanocrystals were intensively studied during the last decade, less information is available for their III-V analogue systems. One reason is that III-V semiconductors are more covalent compounds and high temperatures are usually required for their synthesis. Only a limited number of papers discussing the synthesis and characterization of InP [2–5], GaP [6] and InAs [7,8] nanocrystals appeared in the last years. The strong interest for III-V compounds arises from the expectations that these materials may exhibit even more pronounced quantum size effects than II-VI systems. Thus, III-V materials usually have relatively covalent bonding and direct band gap structure, larger bulk exciton radii and smaller effective masses that makes them promising candidates for various optoelectronic devices. Another important aspects are so-called "green chemical principles" dominating the last years chemistry and it is based on the development of environmentally friendly chemical methodologies and materials [9]. From this point of view III-V compounds like InP are more attractive than the cadmium-related II-VI ones.

A point of special interest is the fabrication of highly luminescent nanocrystals. Therefore the particle surface has to be passivated, *i.e.* surface dangling bonds which give rise to non-radiative recombination have to be saturated for example by organic ligands. In case of InP efficient passivation of the surface requires special treatments. One possibility is etching with certain fluorine compounds.

In this work, we use PES with synchrotron radiation to study InP nanocrystals and their etching with HF with the aim of establishing which chemical bonds exist at the surface and to obtain a better understanding of the etching process. This technique is ideal for acquiring a qualitative understanding of the nanocrystal surface and by recording P 2*p* and In 3*d* core level spectra across a wide range of excitation photon energies we vary the surface sensitivity in our experiment so that variations in the spectra may be identified with surface chemical environments. Conclusions on the degree of surface disorder may be drawn from a large broadening of the surface core-level components relative to the core-level components associated with the interior atoms.

2 Experiment

PES experiments were performed on beamline BW3 of the DORIS III storage ring at HASYLAB/DESY in Hamburg,

---

[a] e-mail: `sorin.adam@desy.de`

Germany. Photoelectron spectra were recorded with an Omicron EA125 hemispherical energy analyzer with normal emission mode and the sample holder was oriented at 45° with respect to the synchrotron light.

Size selected InP nanocrystals were prepared by a standard method resulting "pure" nanocrystals [2,10]. Size determination was done using TEM techniques and optical absorbtion spectra relate the band gap value with the size of the particle using a semi-empirical formula [1]. Those samples have poor photoluminescence efficiency and have to be preserve in protective atmosphere (nitrogen and a dark room) before further treatment.

Sample no. 1 (InP methwash) is the result of washing twice "pure" InP nanocrystals with a solution of toluene:methanol (1:5). The aim of this treatment was to remove the undesirable reaction products that can appear during the synthesis. There are no improvements in the PL yield (0.05%).

Exposure to air and light for many hours conducts to sample no. 2 (InP oxidized).The PL efficiency was slightly increasing but luminescence yield is still low, less than 1%.

A dramatic increase in the photoluminescence yield, more than 20%, occurs after etching the nanoparticles with HF solution under air and illumination conditions [11–13]. Sample no. 3 (InP etched) is a very good candidate for further improvements of the InP nanocrystal optical properties (up to 40% efficiency).

All three samples were deposited from solution on Au films in an N_2 atmosphere and transported to the experiment in sealed flasks. The samples were introduced *via* a fast entry lock into the UHV experimental chamber.

The kinetic energy recorded for P $2p$ and In $3d$ peaks is in the 40−450 eV range. Core-level spectra were fitted to the minimum number of Voigt doublet functions using a complex optimization routine after polynomial+Shirley background subtraction. The spin-orbit splitting value of 0.86 ± 0.01 eV was used for all components in the P $2p$ spectra. This value is in agreement with similar data characterizing the spin-orbit spitting effect for InP bulk samples [14,15].

A total instrumental resolution of 240 meV was used for recording high resolution photoelectron spectra of P $2p$ in the range of 175−578 eV excitation energy. In the high excitation energy range the resolution was allowed to decrease slightly in order to ensure a high count rate in recording the In $3d$ data.

3 Results and discussion

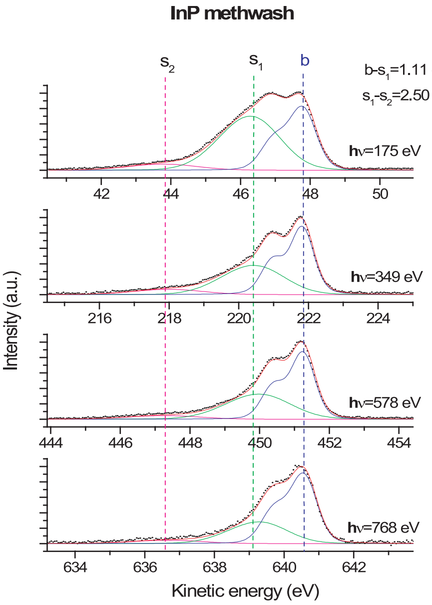

Fig. 1. P $2p$ core-level photoemission spectra of sample no. 1. Component b is due to atoms in the volume of nanocrystals and s_1 and s_2 are surface core-level shifts.

Figure 1 shows P $2p$ core-level spectra recorded through a photon-energy range of 175−768 eV with normalized experimental intensities. Good data fits were possible only with three components for each spectrum with a Lorentzian broadening value of 0.17 eV. Components s_1 and s_2 decrease in relative intensity as the excitation photon energy and subsequence the kinetic energy for photoelectrons increase. These components are, therefore, identified with atoms having a distinct surface environment in the nanocrystal and the component b is due to P atoms in the interior of the nanocrystal volume. Spin-orbit splitting is well resolved in the case of the bulk component b, indicating a high degree of crystallinity inside the nanoparticles and relatively broad surface core-level components s_1 and s_2 are evidence for a large degree of bond length and angle variation at the surface. In this size range up to 30% of the nanocrystal atoms are located on the surface.

Component s_1, shifted by an average value of 1.11 eV to lower kinetic energy with respect to the bulk component b reflects the signal form TOP phosphorus atoms bonding In rich sites at the nanoparticle surface. P dangling bonds located at the surface can contribute to s_1 signal.

The P $2p$ s_2 component indicates a clear P–O bond [16]. An average shift of 3.61 eV relative to the bulk component originates from the phosphorus atoms in TOPO used during the preparation process. Previous studies on bulk InP (110) surfaces showed a rather complicate oxidation process with different chemical structures for phosphorus oxides [17–23]. Signal from an early stage oxidation of clean P surface sites during the sample manipulation and transfer in the UHV chamber (up to 3 min) might contribute to the s_2 component [24].

Dramatic change of the nanocrystal surface occurs after exposure to oxygen. Figure 2 presents a significant increase in intensity for the surface component s_2 relative to s_1. Sample no. 2 presents also a slight increase of the chemical shifts for the surface species. An average of 1.27 eV and 4.27 eV chemical shift relative to the bulk component for the s_1 and s_2 peaks respectively resulted after the fitting procedure. One explanation for the higher shift in binding energy in case of the s_2 contribution is the strong oxidation process resulting after long exposure to air and light (more than 24 h). New P–O bonds with higher binding energy result after the surface reconstruction and P dangling bonds are reduced (passivated) causing also a shift towards lower kinetic energy for component s_1.

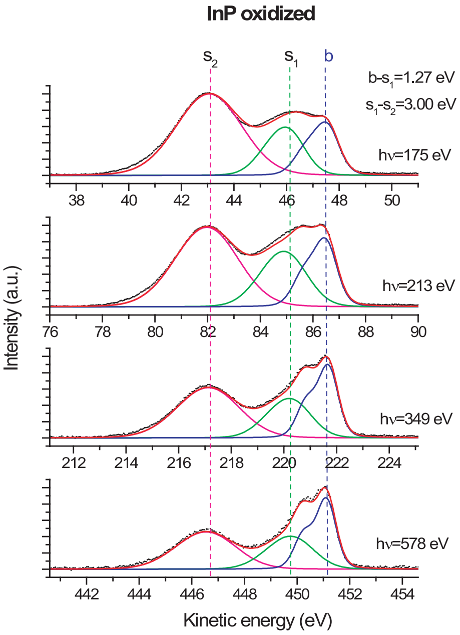

Fig. 2. P $2p$ signal from sample no. 2. There are important variations in intensity for the s_1 and s_2 surface contributions due to exposure to air.

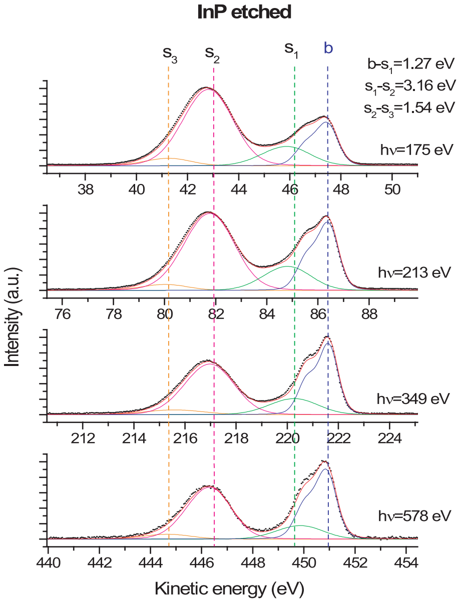

Fig. 3. In case of InP sample no. 3 there is an evidence for a third surface component s_3 due to the etching treatment.

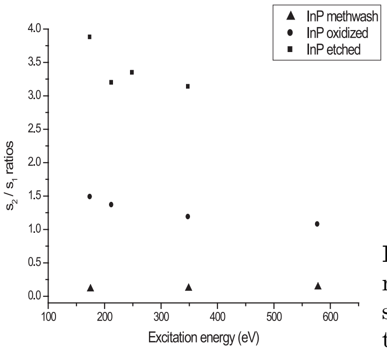

Fig. 4. s_2/s_1 intensity ratios of InP nanocrystal samples at different excitation energies.

For both previous samples the room temperature quantum efficiency is still very low. This is the result of non-adequate passivation of the nanocrystal surface. The dangling bonds may act as traps for the photogenerated carriers and can provide non-radiative recombination pathways.

Post-preparative modification of the particle surface provide a way to eliminate those undesirable trap sites. A recent method implying the treatment of InP nanocrystals with HF solution results in a strong band edge luminescence. Figure 3 presents the P $2p$ core-level spectra after the etching procedure with HF. In addition to surface components s_1 and s_2 discussed before, a new feature, the s_3 component appears indicating the presence of F atoms on the nanocrystal surface. There are also changes in relative intensity for the other two surface contributions, increasing and decreasing for s_2 and s_1 respectively. It might be possible that HF removes P atoms with surface dangling bonds that are not well passivated with organic ligands. Once such atoms are removed, the remaining site, reach in In, can be capped with TOPO ligands and also with fluorine. Better surface passivation results in a drastic increase of the photoluminescence quantum yield.

The evolution of the s_2/s_1 ratios for all three samples *versus* excitation energy are plotted in Figure 4. For all three samples the s_2/s_1 ratios show only small variation once the excitation energy takes different values. This result is in agreement with the assumption that components s_1 and s_2 represent signal from genuine surface environments. Instead, there are strong ratio variations in case of different treatments and increasing in s_2/s_1 ratio has a direct but nonlinear response in the improving of PL efficiency. The nonlinear response in the PL yield could be explained by the fact that generally, already few unpassivated surface sites can lead to poor PL properties. A very good passivation of the nanocrystal surface results in a huge increase of the PL yield.

The HF treatment in presence of light activates a chemical reaction that removes unpassivated P sites (dangling bonds) from the nanocrystals surfaces. Once those atoms are removed, the resulting environment is capped with TOPO ligands or fluorine. This would also explain high P $2p$ s_2/s_1 ratios after the etching treatment.

The In $3d_{5/2}$ spectra are more difficult to fit using a standard procedure because of the decreasing instrumental resolution due to the necessity of using high excitation energy combined with the low count rate. There is also the "physical" aspect-small chemical shifts in case of surface oxidation or HF etching treatment for In sites. One approach in case of In $3d$ investigation might be simply to overlap intensity normalized spectra of two different samples (methwash and etched) irradiated with the same photon energy. Figure 5 shows for the surface sensitive regime (50 to 60 eV kinetic energy) a much broader In $3d_{5/2}$ spectrum for the etched InP sample relative to the methanol-wash one. Sharper feature in case of the sample washed with methanol (sample no. 1) results from the important presence of the TOP ligands at the nanocrystals surface and possible bonds with In surface atoms (In–P bonds) creating a bulk InP like signal in the spectrum. Only In–O bonds (mainly with TOPO ligands) and free In atoms at the surface might contribute to the

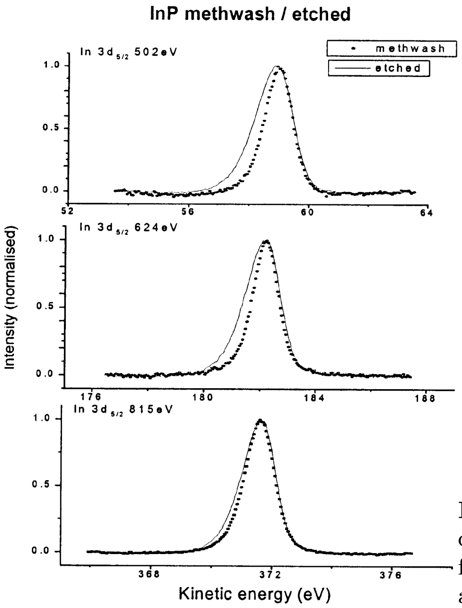

Fig. 5. In $3d_{5/2}$ core-level spectra for samples no. 1 and 3.

experimental broadening but the number of these sites is limited as shown by the previous P $2p$ data. According to In core-level studies on InP (110) clean and oxidized surface the chemical shifts value in those cases should be about 0.32 ± 0.04 and 1.1 ± 0.4 eV to lower kinetic energy respectively [14,15,17,23]. The same hypotheses can be applied in case of etched sample (sample no. 3). Now the bulk like signal is reduced due to decreasing presence of TOP molecule on the InP nanoparticle surface. On the other hand the surface oxidation is more intense and together with In–F bonds increase the broadening for In $3d$ peaks. It should be noticed once again the good agreement with the P $2p$ results.

For a more bulk sensitive regime (365–380 eV KE) the broadening for the both sample decreases due to the enhanced contribution of bulk atoms at the photoelectron yield.

4 Summary

In spite of the large degree of structural disorder at the surface it is possible to give a general description of the chemical bonds that are present on the top most layer of nanocrystals. There is a direct relation between the intensity ratios for the surface sites s_1 and s_2 of P $2p$ spectra and the PL efficiency. When the intensity of the s_1 component associated with P in TOP and with surface P atoms having dangling bonds is reduced in favor of the component s_2 corresponding to P in TOPO, the photoluminescence quantum yield increases. Our results indicate that the HF treatment removes the unpassivated P sites simultaneously with a significant enhancement of TOPO ligands present at the particle surface. The reduction of dangling bonds and the improved surface passivation suppress non-radiative recombination in favor of high photolumine sequence. Recent results reveal up to 40% photoluminescence quantum efficiency for some of InP etched nanocrystals. Additional experiments are required to obtain reproducible high luminescence results and to a better understanding of photoetching process.

References

1. D. Bertram, O.I. Micic, A.J. Nozik, Phys. Rev. B **57**, R4265 (1998)
2. O.I. Micic, C.J. Curtis, K M. Jones, J.R. Sprague, A.J. Nozik, J. Phys. Chem. **98**, 4966 (1994)
3. A.A. Guzelian, J.E.B. Katari, A.V. Kadavanich, U. Banin, K. Hamad, E. Juban, A.P. Alivisatos, R.H. Wolters, C.C. Arnold, J.R. Heath, J. Phys. Chem. **100**, 7212 (1996)
4. O.I. Micic, K.M. Jones, A Cahill, A.J. Nozik, J. Phys. Chem. **102**, 9791 (1998)
5. O.I. Micic, S.P. Ahrenkiel, A.J. Nozik, Appl. Phys. Lett. **78**, 4022 (2001)
6. O.I. Micic, J.R. Sprague, C.J. Curtis, K.M. Jones, J.L. Machol, A.J. Nozik, H. Giessen, B. Fluegel, G. Mohs, N. Peyghambarian, J. Phys. Chem. **99**, 7754 (1995)
7. U. Banin, C.J. Lee, A.A. Guzelian, A.V. Kadavanich, X. Peng, A.P. Alivisatos, W. Iakolski, G.W. Bryant, A.L. Efros, M. Rosen, J. Chem. Phys. **109**, 2306 (1998)
8. C. McGinley, M. Riedler, T. Möller, H. Borchert, S. Haubold, M. Haase, H. Weller, Phys. Rev. B **65**, 245308 (2002)
9. X. Peng, Chem. Eur. J. **8**, 335 (2002)
10. R.L. Wells, C.G. Pitt, A.T. McPhail, A.P. Purdy, S. Schafieezad, R.B. Hallock, Chem. Matt. **1**, 4 (1989)
11. D. Talapin. Ph.D. thesis, University of Hamburg, 2002
12. O.I. Micic, J.R. Sprague, Z. Li, A.J. Nozik, J. Appl. Phys. Lett. **68**, 3150 (1996)
13. O.I. Micic, Fu.H. Cheong, A. Zunger, J.R. Sprague, A. Mascarenhas, A.J. Nozik, J. Phys. Chem. **101**, 4904 (1997)
14. T. Kendelewicz, P.H. Mahowald, K.A. Bertness, C.E. McCants, I. Lindau, W.E. Spicer, Phys. Rev. B **36**, 6543 (1987)
15. W.G. Wilke, V. Hinkel, W. Theis, K. Horn, Phys. Rev. B **40**, 9824 (1989)
16. J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray photoelectron Spectroscopy*, edited by J. Chastain (Perkin-Elmer, Eden Prairie, MN, 1992)
17. G. Hollinger, E. Bergignat, J. Joseph, Y. Robach, J. Vac. Sci. Technol. A **3**(6), 2082 (1985)
18. K.A. Bertness, T. Kendelewicz, R.S. List, M.D. Williams, I. Lindau, W.E. Spicer, J. Vac. Sci. Technol. A **4**(3), 1424 (1986)
19. G. Hughes, R. Ludeke, J. Vac. Sci. Technol. B **4**(4), 1109 (1986)
20. G. Hollinger, J. Joseph, Y. Robach, E. Bergignat, B. Commere, P. Viktorovitch, M. Froment, J. Vac. Sci. Technol. B **5**(4), 1108 (1987)
21. K.A. Bertness, J.J. Yeah, D.J. Friedman, P.H. Mahowald, A.K. Wahi, T. Kendelewicz, I. Lindau, W.E. Spicer, Phys. Rev. B **38**, 5406 (1988)
22. D. Gallet, G. Hollinger, C. Santinelli, L. Goldstein, J. Vac. Sci. Technol. B **10**(4), 1267 (1992)
23. M. Losurdo, P. Capezzuto, G. Bruno, J. Vac. Sci. Technol. B **14**(2), 691 (1996)
24. G. Hollinger, G. Hughes, F.J. Himpsel, J.L. Jordan, J.F. Morar, F. Houzay, Surf. Sci. **168**, 617 (1986)