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Evidence for surface reconstruction on InAs nanocrystals

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By means of photoelectron spectroscopy with synchrotron radiation we have studied the surfaces of colloidally prepared InAs nanocrystals in the 30–60 Å size range. We find evidence that specific surface states exist for both In and As atoms and that the passivating trioctylphosphine ligands form chemical bonds with a fraction of the surface In and As atoms. There is evidence for a significant amount of bond-length variation at the nanocrystal surface.

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I. INTRODUCTION

Colloidally prepared semiconductor nanocrystals show size dependant scaling laws for their optical, electronic, thermal, and mechanical properties.[1–4] For III-V nanocrystals size effects are most striking in the size range of 20–60 Å and since a large number of atoms are either on or influenced by the surface, knowledge of the structural and electronic properties of this surface is crucial for a complete description of various nanocrystal properties. Modification of the surface dramatically increases nanocrystal luminescence, which combined with the band-gap size dependence is leading to new technologies such as nanocrystal optical displays,[5] lasers,[6] and biological labeling.[7] Surface modification may either involve oxidation[8] or the growth of an epitaxial shell layer around the nanocrystal[9] both of which remove surface states that lie in the band gap. It would be useful to clarify the chemical nature of these surface states in order to further improve techniques of luminescence enhancement in nanocrystal applications.

At present, very few studies on III-V nanocrystal surfaces exist. Hamad *et al.* interpreted the broadening of x-ray appearance near-edge structure spectra features as being due to structural disorder allied to a bond-length variation, which is caused by a surface relaxation similar to that found on the III-V (110) clean surfaces (Ref. 10). ^{31}P nuclear magnetic resonance experiments found that the organic ligands have many distinct surface bonding environments most probably due to the different chemical environments associated with different crystal planes.[11] This is because III-V nanocrystals are approximately spherical and so the surface comprises a collection of low index planes meeting at complex line defects. Many established surface science techniques are not sensitive to the surface modification of the crystal structure in nanocrystals. This is either due to lack of long-range order for diffraction techniques or else due to the ligand coverage that would hinder probe microscopy in a surface structural study. Also, transmission electron microscopy (TEM) images of high resolution[12] do not reveal any clear surface detail.

In this work, we use photoelectron spectroscopy (PES) with synchrotron radiation to study InAs nanocrystals with the aim of establishing which chemical bonds exist at the surface. This technique is ideal for acquiring a qualitative understanding of the nanocrystal surface and has been used by Winkler *et al.* to fully describe chemical bonding on nanocrystalline CdS surfaces.[13,14] By recording In $4d$ and As $3d$ core-level spectra across a range of photon energies we vary the surface sensitivity in our experiment so that variations in the spectra may be identified with surface chemical environments. These surface core-level shifts may be compared with those found for low index InAs clean surfaces so as to establish the nature of the surface chemical bonds. A complimentary investigation records equivalent spectra for different nanocrystal sizes. Variation of the surface to bulk atomic ratio in this way confirms the presence of genuine surface core-level shifts. 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. Relatively broad surface core-level shifted components are evidence for a large degree of bond length and angle variation across the surface when compared to the precise values for chemical bonds in the interior of the system.

II. EXPERIMENT

Core-level photoelectron spectra were recorded at beamline BW3 of the DORIS III storage ring at HASYLAB in Hamburg. Size selected, trioctylphosphine (TOP) passivated InAs nanocrystals were prepared by a standard method.[15] It is the phosphorous atom of the TOP molecule which bonds to the nanocrystal surface. Size determination was done using TEM and optical absorbtion spectra confirmed that the band gap scaled with nanocrystal size in agreement with Ref. 15. Nanocrystals were deposited from solution on Au films in an N_2 atmosphere and transported to the experiment in sealed flasks. These samples were introduced, via a fast entry load lock, into the UHV chamber that was equipped with an Omicron EA125 hemispherical electron spectrometer. A plane grating Zeiss SX700 monochromator selected photons in the 70–600 eV energy range and As $3d$ and In $4d$ core-level photoelectron spectra were thus recorded with kinetic energies in the 40–550 eV range. The combined photon and electron spectrometer resolution were set to 200 meV for

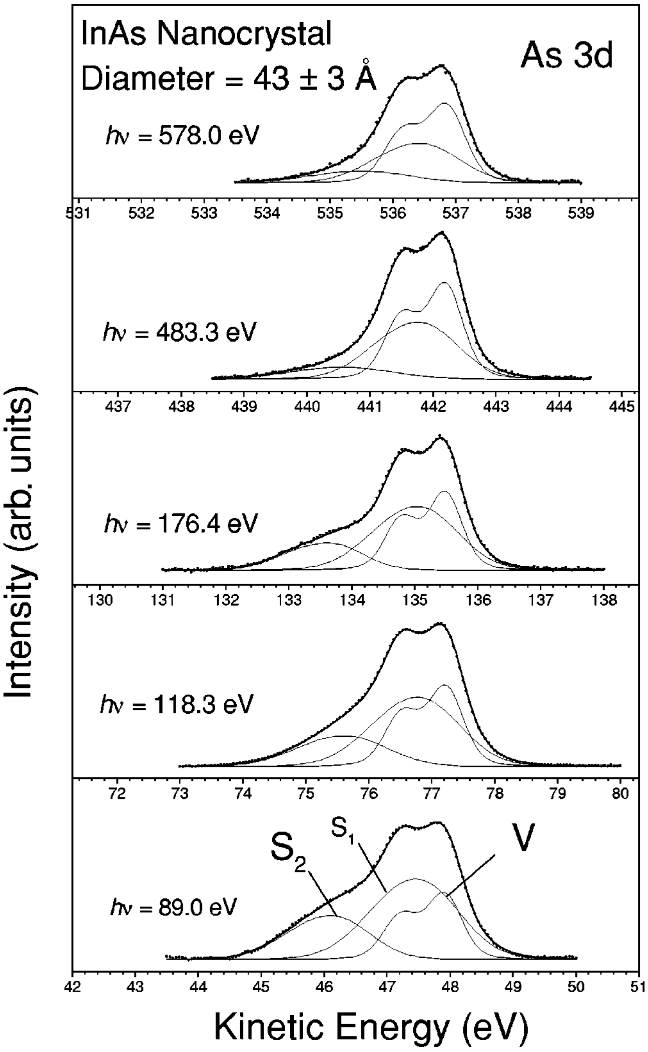

FIG. 1. As $3d$ core-level photoemission spectra recorded at various energies for nanocrystals 43 ± 3 Å in diameter. The sum of the Voigt functions reproduces the experimental data that are shown as dots. Component *V* is due to atoms in the volume of the nanocrystals and S_1 and S_2 are surface core-level shifts.

spectra recorded using photon energies below 200 eV. Above this energy the resolution was allowed to decrease slightly, which allowed us to ensure a high count rate in recording the data. This resolution decrease had a negligible effect on our fitting accuracy.

Core-level spectra were fitted to the minimum number of (spin-orbit split) Voigt functions using a simplex optimization routine after polynomial background subtraction. Spin-orbit splitting values of 0.85 eV and 0.69 eV, respectively, were used for all components in the In and As spectra even when surface broadening was so large that this splitting was unresolved. Values for the Lorentzian broadening of 0.155 and 0.17 for In and As spectra, respectively, were also held fixed for all components during fitting but the branching ratio varied between 0.64 and 0.83 across the photon energy range, as expected.[16,17] The fixed parameters used here are in agreement with earlier photoemission studies on various InAs (Refs. 18,19) or GaAs (Ref. 20,21) surfaces. Gaussian broadening of the various components are given below for spectra recorded using a photon energy of 89.0 eV. At the higher photon energies in all spectra this broadening increases slightly due to an increase in the photon broadening as mentioned above.

III. RESULTS AND DISCUSSION

As $3d$ core-level spectra recorded from a film of nanocrystals with a diameter of 43 ± 3 Å are shown in Fig. 1. Through the photon energy range shown good data fits were possible only with three components for each spectrum. The Voigt component of highest kinetic energy (*V*) is a well resolved spin-orbit (0.69 eV) split doublet while the two components at lower kinetic energy (S_1 and S_2) are so much broader that the spin-orbit splitting is unresolved. The Gaussian widths are 0.60, 1.20 ± 0.05, and 1.20 ± 0.20 eV of these Voigt functions, respectively, in the spectrum recorded at 89.0 eV. Components S_1 and S_2 increase in relative intensity towards the lower photon energies as the photoelectron kinetic energy is tuned toward the maximum in surface sensitivity. These components are, therefore, identified with atoms having a distinct surface environment in the nanocrystal and the component *V* is due to As atoms in the interior of the nanocrystal volume.

That the As $3d$ core level components S_1 and S_2 in Fig. 1 are genuine surface core-level shifts is confirmed by data recorded from nanocrystals of different sizes. Figure 2 shows As $3d$ core-level spectra for nanocrystals of three different diameters at both surface and volume sensitive photon energies. With increasing nanocrystal size the intensity of the surface components (S_1 and S_2) reduce in intensity with respect to the volume component *V*. This is simply due to the decrease of the surface to volume ratio with increasing size for any approximately spherical particle.

The As $3d$ component S_1 is shifted by 0.22 eV to lower kinetic energy/higher binding energy with respect to the volume component *V*. In clean surface studies such a shift has been associated with excess or bulklike As at the surface and is similar although smaller in magnitude to surface core-level shifts (SCLS's) found for As trimers on the (111) B-(2×2)III-V surfaces.[19,21] Component S_1 therefore might be identified with a similar As-As bond derived surface structure present on the collection of low index planes and possibly at the line defects between them, which make up the nanocrystal surface. An As $3d$ SCLS of similar broadening relative to the volume component *V* and shifted to 0.10 eV lower kinetic energy is observed in the initial stages of oxidation of a GaAs(110) surface.[22] We include this possibility here as the samples have been exposed to air for ~1 min. but we cannot exclude As-As chemical bond already mentioned. This oxidation dose is not extreme due to the ligand protection as judged from optical absorption data. On the (110) surface the As $3d$ SCLS induced by oxidation is due to surface As that prior to oxidation has the s^2p^3 bonding orbital configuration. The relevant SCLS is to the *higher* kinetic energy side of the volume peak. These atoms are back bonded to three cations in the layer below and have a filled lone pair oriented normal to the surface. We assume here that

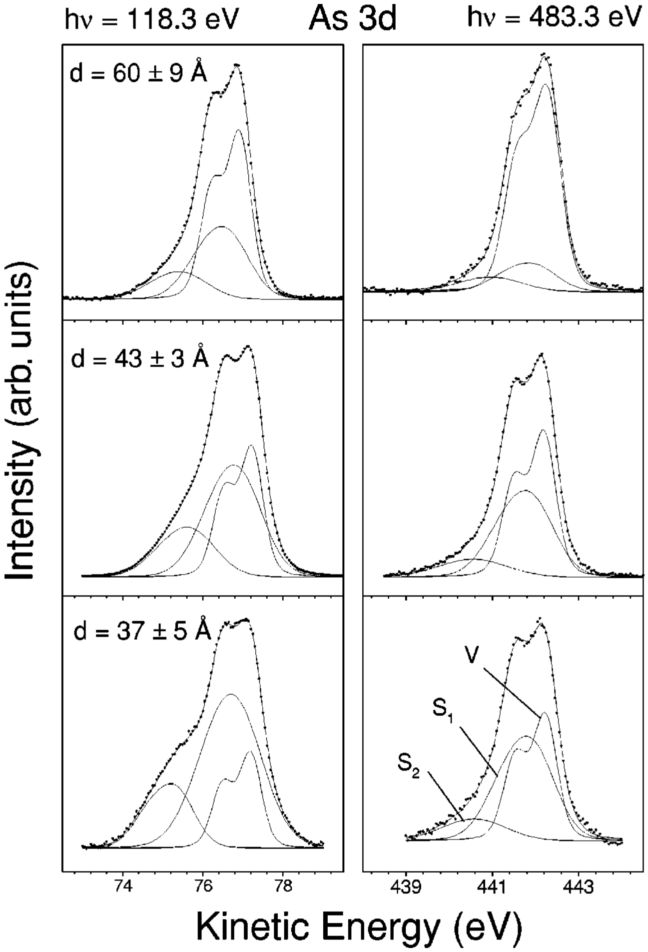

FIG. 2. As 3d core-level spectra recorded at two photon energies for three different nanocrystal sizes. Intensity variations in the Voigt components are found for changes in both photon energy and nanocrystal size.

if such a (110)-like surface state exists in nanocrystals in solution it is removed by oxidation during the sample transfer.

Component S_2 in these spectra is here associated with those surface As atoms bonded to the passivating organic ligands TOP. The magnitude of this SCLS is large with some uncertainty at 1.4 ± 0.3 eV implying that a significant amount of charge is transferred from the surface As atom to the P atom at the end of the ligand chain to which it is bonded. Such an As atom may itself be back bonded to two or three In or possibly As atoms or a mixture of both. Many bonding possibilities are certain to exist on a multifaceted surface and this will in turn lead to a large broadening of the surface core-level components as is observed here. This is discussed below for all core-level spectra in relation to surface roughening in general.

Photoelectron spectra of the In 4d core level for the sample with nanocrystals of diameter 43 ± 3 Å are shown in Fig. 3. In their decomposition into Voigt components these are qualitatively similar to the As 3d spectra described above. We have fitted three components: a volume component V where the spin-orbit splitting of 0.85 eV is again well resolved and two much broader surface components labeled S_1 and S_2. The Gaussian broadening for these components are 0.65, 1.90 ± 0.10, and 1.60 ± 0.10 eV, respectively, for data recorded at 89.0 eV. The photon energy dependence confirms, as for As 3d above, that the lower kinetic energy components originate from In atoms at the nanocrystal surface. The extreme broadening of the SCLS's is as pronounced as for the As 3d core-level spectra but the magnitudes of the shifts are larger. S_1 is at 0.44 eV to lower kinetic energy relative to the volume component V and S_2 is shifted by 2.4 ± 0.1 eV.

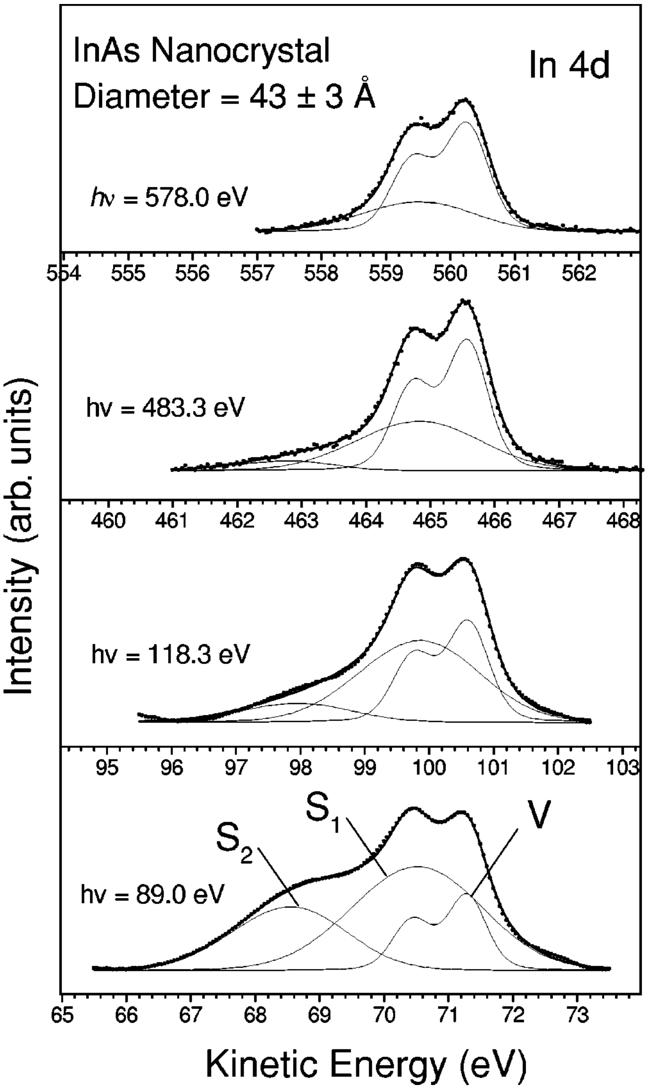

FIG. 3. In 4d core-level spectra recorded at photon energies also used to collect the As 3d data of Fig. 1.

Component S_1 is reminiscent (although with a slightly larger shift in energy of ~ 0.15 eV relative to component V) of the In 4d SCLS found for the InAs (110) clean surface.[18] It is also similar to a component in the Ga 3d spectra of the GaAs (100) (4×2)-$c(8 \times 2)$ surface,[20] which was due to Ga dimers where both atoms were back bonded to two As atoms in the layer below. More recent work has shown that subsurface group III dimers are energetically more favorable on the group III rich surfaces,[23,24] but for comparison with nanocrystal surfaces it is the hybridization of the surface atom bonding orbitals, which we wish to establish here. These systems have similar local bonding, i.e., a planar sp^2 hybridization for the bonding orbitals[25] and are each bonded to three surface atoms. A similar SCLS in Ga $3d$ spectra from the GaAs$(311)A$ was associated with surface defects[26] but we favor the similarity with the (110) surface core-level shift as this crystal face has the lowest surface energy and is probably predominant among the crystal planes that make up the nanocrystal surface.[10] We include also the likelihood of oxidation contributing to this component as we suggested for the As $3d$ core levels above: component S_1 is similarly broad and shifted only to a slightly higher energy than the surface oxidized component of GaAs(110).[22] Prior to oxidation the surface Ga had the sp^2 hybridization already described lending further weight to our description of the surface despite the effects of oxidation. We identify component S_2 in Fig. 3 with In-P bonds at the nanocrystal/TOP interface.

We have therefore a description of the chemical bonds present at the InAs nanocrystal surface. To summarize, TOP ligands are bonded to both In and As surface atoms, surface In atoms exist with sp^2 hybridization and for As there is a surface environment but our results cannot distinguish between As-As bonds and As-O bonds formed at s^2p^3 "lone pair" surface As. As-As surface bonding was suggested by Banin *et al.* to account for size disparity when TEM and STS data were compared[27] but the As s^2p^3 surface state is favorable as it essentially receives the valence charge that is necessarily surplus to the In sp^2 surface state.[28] This is the "electron counting" interpretation of stable III-V surfaces[29] and we believe it should apply here. In general, we have good evidence that the local bonding structure found for the (110) plane is present on a significant part of the nanocrystal surface.

We have emphasized the extreme broadening of the surface core-level shifts. This is not exclusively due to inhomogeneous pinning of the Fermi level by defects at different surface sites. Such a process would broaden all core-level components to the same degree but the volume core-level component is relatively sharp in all spectra. The pinning effect *does* exist to the extent that the volume component is broadened (by ~ 0.3 eV) relative to that found for clean surface studies with similar experimental resolution. But the further broadening of the surface components is due mainly to surface roughness. A similar effect was observed for the interaction of S with the GaAs$(111)A$ surface[30] where surface shifted peaks for both Ga $3d$ and As $3d$ spectra had Gaussian broadening two to three times larger than those of the bulk derived photopeaks despite the fact that scanning tunnel microscope images of the same surface revealed some degree of crystalline order. The relative surface broadening in photoemission for that system is of the same magnitude as that observed here. We conclude that although there are a large number of defects at the nanocrystal surface the form of the chemical bonds present is qualitatively described.

The surface core-level shifts (S_2) that we associate with As-P and In-P chemical bonds are large, 1.4 ± 0.3 eV and 2.4 ± 0.1 eV, respectively. We can be certain from the size of these shifts that they are not caused solely by charge transfer from the surface atoms to the TOP molecules. Such large core-level shifts give strong evidence for quite severe distortion of the crystal at the surface. To effectively lose valence charge such that the core electrons have such increased binding energy, the As and In atoms bonded to TOP should have severely distorted bond lengths and bond angles in comparison to those of the volume atoms. Any oxidation may also affect the exact size of these energy shifts but we may at least be sure that the binding of TOP to both In and As causes significant distortion in the chemical bonding at the surface. We note also that this distortion may also be different for nanocrystals forming a thin film as opposed to those in solution.

It should be noted that some degree of strain is expected in the ligand-surface bonds in nanocrystals. This has been given as an explanation for thermally induced luminescence quenching in CdSe nanocrystals where heating generates surface charge traps in the ligand-surface bonds.[31] It is the strain in these bonds which make this process possible and we here have evidence that for InAs nanocrystals a similar strain (inferred from the large values of the S_2 SCLS's) in chemical bonds exists at the surface. A related point is the discovery that zinc-blende nanocrystals have a dipole moment that scales with the particle size.[32] The magnitude of this effect is strongly effected by the degree of surface reconstruction[33] and this is extreme for InAs nanocrystals as implied by the size of the SCLS's described above. These two phenomena of a dipole moment and thermally induced luminescence quenching are explained by surface charging effects that would be made possible by the existence of an unusually strained surface crystal structure. These findings are consistent with what we have described here, that is, a large degree of surface strain in nanocrystals. Such strain we believe is evidenced by the extent of bond-length variation which we propose to explain the broadening of the surface core-level shifts. Surface structure and its relationship to charging of the nanocrystal surface is an interesting study as it points toward a general description of the electronic properties of a highly complex surface.

IV. SUMMARY

We have shown that core-level photoemission spectroscopy is useful in describing the nature of III-V nanocrystal surfaces. TOP is bonded to surface In as would be expected but also to surface As atoms. We also see that there is a large degree of structural disorder at the surface. In spite of this we can give a general description of which chemical bonds are present and show that the surface atoms exhibit bonding orbital rehybridization that is typical for all reconstructed semiconductor surfaces.

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