

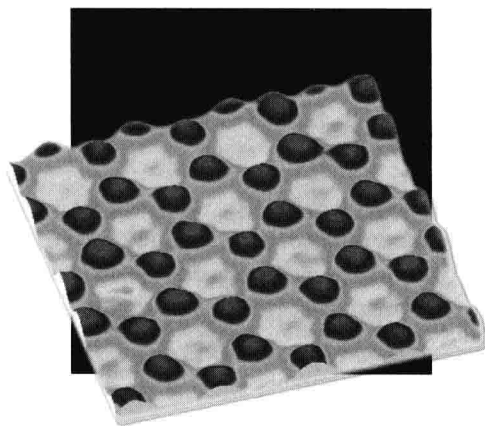
Proceedings of the Workshop on
Synchrotron Radiation
and **Nanostructures**

Papers in Honour of Paolo Perfetti

Antonio Cricenti
Giorgio Margaritondo

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SYNCHROTRON RADIATION AND NANOSTRUCTURES

Proceedings of the Workshop

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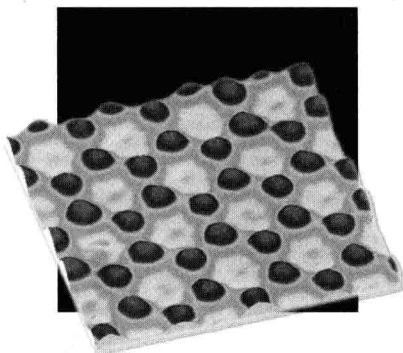
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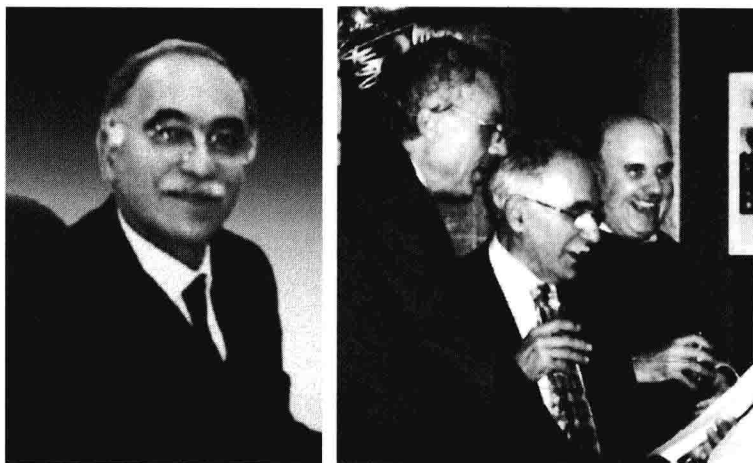
PREFACE

This book is dedicated to Paolo Perfetti an outstanding scientist and a wonderful friend. It is a collection of articles that were presented at the Workshop on Synchrotron Radiation and Nanostructures, held in Rome in November 2008 — that was also in the honor of Paolo and attracted many of his friends worldwide.

Paolo Perfetti, in a long and illustrious career, made fundamental contributions to the development of synchrotron radiation and scanning probe microscopy and to their applications in materials science and biology. It would take a whole book to describe in detail his many results in a variety of domains. Hence we could only note some of the most important ones here.

As early as 1971, Paolo pioneered molecular beam epitaxy (MBE), then a technique in its infancy and almost unknown outside the USA. Not even the name was universally known and used, so Paolo developed one of the first systems worldwide under a different name: “Bis technique” after R. F. Bis, author of early work in the epitaxy of lead chalcogenides (R. F. Bis *et al.*, *J. Vac. Sci. Technol.* **9**, 226 (1972)). During the same period, he became interested in semiconductor heterojunctions and their interface properties. One of the earliest works witness the shift of a then very young Federico Capasso from laser research to a bright career in interface engineering (P. Perfetti, M. Antichi, F. Capasso and G. Margaritondo, *Infrared. Phys.* **14**, 255 (1974)).

Working in Berkeley in collaboration with David Shirley, Paolo invented a new and very productive line of research: the use of photoemission to measure heterojunction band discontinuities (P. Perfetti, D. Denley, K.A. Mills and D.A. Shirley, *Appl. Phys. Letters* **33**, 66 (1978)). Many scientists adopted this approach in the following decades. This was also one of the milestones in the development of synchrotron radiation and specifically of synchrotron-based photoemission.



Paolo Perfetti: a formal appearance at his office (left) and a more informal version as a “fraschetta” singer with the editors of this book (right).

Synchrotron radiation remained a key element of Paolo’s career for more than 30 years and made him famous throughout the world. His synchrotron-based contributions include photoemission, spectro-microscopy, X-ray diffraction, X-ray absorption and EXAFS — and span diverse subdomains from solid interface formation to catalysis.

The natural continuation of Paolo’s work in synchrotron radiation was his more recent activity in free electron laser (FEL) science. He contributed to the first use of FELs in scanning near-field microscopy (A. Cricenti *et al.*, *Appl. Phys. Letters* **73**, 151 (1998)). He was a moving force then for the new giant Italian FEL projects SPARC and SPARX.

The research work of Paolo was not limited to synchrotron radiation and FEL techniques: his search for new phenomena and of their explanation brought him to master different tools such as electron energy loss, inverse photoemission, neutron experiments, laser deposition and Kelvin probe analysis. In recent years, he increasingly worked on problems outside the traditional boundaries of physics: neurobiology, physiology and other biomedical subdomains.

Paolo is not only an outstanding scientist and a pioneer of new techniques, but also a science leader. He was a key person in the development of the Frascati synchrotron project (PULS). For many years (1987-2008), he was the Director of the Istituto di Struttura della Materia (ISM) of the Consiglio Nazionale delle Ricerche (CNR) in Rome, Italy — a reference worldwide for solid state physics, interface science, novel microscopies and other domains. The workshop that led to this book was also to celebrate his retirement after 21 years of leadership.

We are very happy to honor him with this volume, containing a collection of contributions from his present and former co-workers, as well as from friends in the scientific community. This is our way to thank him for his friendship, enthusiasm and human wisdom. He is an example of rigor, honesty and dedication to science.

The workshop took place in November 21, 2008 at the CNR Research Area of Tor Vergata, Rome, Italy. It was attended by 75 scientists from seven countries. Others who could not personally attend sent personal messages, greetings and best wishes to Paolo. The day was crowned by wine and “porchetta” at a Frascati “fraschetta”, accompanied by bawdy Roman songs to which Paolo participated with great enthusiasm (offsetting his objectively limited singing skills).

The workshop’s objective was to present the capabilities of state-of-the-art synchrotron radiation and scanning probe microscopy techniques, together with general theory work, in elucidating the fundamental electronic and structural properties of semiconductor and metal surfaces, interfaces, nanostructures, layers and diverse biological systems.

We are grateful to the workshop sponsors, the Department of Materials of CNR and the Ecole Polytechnique Federale de Lausanne (EPFL). We also wish to thank all the staff members of the ISM-CNR for the excellent support, organization and hospitality.

Antonio Cricenti
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ADSORPTION OF CYCLOPENTENE ON GaAs(001) AND InP(001), A COMPARATIVE STUDY BY SYNCHROTRON-BASED CORE LEVEL SPECTROSCOPY

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Keywords: Synchrotron x-ray photoelectron spectroscopy, SXPS, organic molecules, InP(001), GaAs(001), (2×4) III-V semiconductors, cyclopentene

1. Abstract

The interface formation between cyclopentene and the (2×4) reconstructed GaAs(001) and InP(001) surfaces has been studied by soft X-ray photoemission spectroscopy (SXPS). After preparation of an uncontaminated (2×4) reconstruction under ultra-high vacuum (UHV) conditions the surfaces were exposed to cyclopentene. The changes in the In 4d and P 2p, as well as the Ga 3d, As 3d and C 1s, core level emission lines indicate a covalent bonding of cyclopentene to the topmost atoms of these surfaces. Based on these results and due to the comparison between the results for the different III-V semiconductors, two different adsorption structures of cyclopentene are found. Our results suggest that cyclopentene adsorbs onto the InP(001) (2×4) surface by the formation of two bonds, in a cycloaddition-like reaction. For the adsorption of cyclopentene on the GaAs(001) (2×4) surface, only a single bond formation is found. The difference in the adsorption structures are explained by the different dimer configurations of the substrate surfaces.

2. Introduction

Synchrotron based photoemission spectroscopy (SXPS) is suitable for the investigation of clean reconstructed semiconductor surfaces as well as for the characterization of the interface formation between organic molecules and such surface reconstructions. This method can help to elucidate bonding configurations based on the analysis of core level emission line shapes, the identification of surface core level components and the chemical composition of the surface. Therefore, adsorption structures of organic molecules on semiconductor surfaces are presented based on SXPS data. By the understanding of the interface formation of such heterostructures, new applications can be developed or improved. Since organic molecules can be synthesized chemically, we can choose from a large variety of organic molecules in terms of structure and functionality.¹⁻³

Until now, most results concern the interface formation between organic molecules and the Si(001)(2 × 1) reconstructed surface.^{1,2,4-12} In that context, it was shown that the surface dimer structure is a basic prerequisite for the bonding mechanism. For example, a bonding via a [2 + 2]-cycloaddition reaction is only allowed for a bonding on an asymmetric surface dimer, which is the case for the Si(001)(2 × 1) surface.^{2,13,14} In order to clarify the role of the surface dimer structure on the bonding mechanism, investigations of molecule adsorption on different dimer configurations are necessary. Such different dimer configurations are provided in our investigations by GaAs(001) and InP(001) surfaces,^{15,17} as can be seen in Fig. 1.

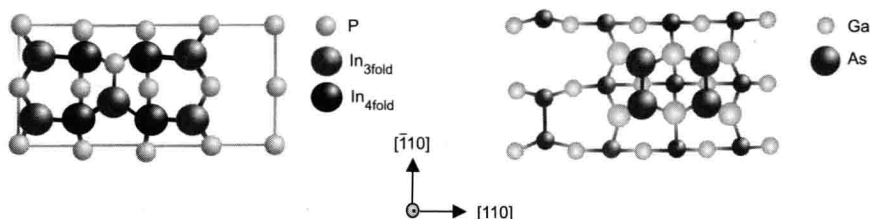


Fig. 1. On the left: topview of the InP(001)(2 × 4) surface reconstruction. On the right: topview of the GaAs(001)(2 × 4) surface reconstruction.

The atomic structures of the clean reconstructed InP(001)(2 × 4) and the GaAs(001)(2 × 4) surfaces have been investigated in recent years. The InP(001)(2 × 4) surface is well described by the so-called asymmetric ‘mixed-dimer’ model, a structure that consists of an In-P hetero-dimer with a filled dangling bond at the P atom and an empty dangling bond at

the In atom.^{16,17} These dimer atoms are bonded to fourfold coordinated second layer In atoms. The outer In atoms of the second layer are threefold coordinated.

For the GaAs(001)(2 × 4) the topmost layer consists of As atoms forming dimers with double occupied dangling bonds which are bonded to second layer Ga atoms.¹⁸

Core level spectroscopy was performed to investigate the interface formation between the III-V (001) surfaces and cyclopentene. Numerical analysis of the In 4d, P 2p, Ga 3d, As 3d and C 1s core level emission lines by best fit reveals information on the interface formation. Additionally, reflectance anisotropy spectroscopy (RAS) measurements were performed to monitor the deposition process. Based on the experimental results, structure models for the cyclopentene-surface linkage on the two (2 × 4) reconstructed surfaces, the InP(001)(2 × 4) and the GaAs(001)(2 × 4) surfaces, were developed.

3. Experimental

The Sb-doped InP(001) samples, investigated here, were grown by metal-organic vapour phase epitaxy (MOVPE) using phosphine (PH₃) and trimethylindium (TMIn) as precursors. Directly after growth, the samples were capped with an amorphous phosphorous/arsenic double layer by photo-decomposition of PH₃ and AsH₃ in the MOVPE reactor.¹⁹ The GaAs(001) samples used in this work were Si-doped (nominal $n = 5 \times 10^{17} \text{ cm}^{-3}$), grown by molecular beam epitaxy (MBE) and capped with amorphous arsenic directly after growth using an As₂ flux.²⁰

After transfer of the samples to UHV, contamination free and well ordered (001) surfaces were prepared by heating to approximately 400°C(±20°C) for 15 min for InP and to 420°C(±20°C) for 15 min for the GaAs(001)(2 × 4). After this procedure the surface reconstructions were determined by low energy electron diffraction (LEED) showing a clear (2 × 4) pattern in both cases. The base pressure throughout all experiments was below 2×10^{-10} mbar.

Cyclopentene with a purity higher than 97% was introduced from gas phase into the chamber using a variable gas-inlet valve. During the deposition, the samples were held at room temperature (RT). In order to avoid decomposition of the molecules, all filaments inside the chamber, e.g. ion gauges, were switched off during the exposure. The effective cyclopentene layer thickness was estimated from SXPS measurements to be approximately one monolayer. The whole deposition process was monitored by

RAS.

Synchrotron based photoemission measurements were performed at the Russian-German beamline (RGBL) at the synchrotron facility BESSY II. The spectra were taken in normal emission with a total instrumental resolution (beamline plus analyser) of 120 meV at an excitation energy of 75 eV. Kinetic energies (binding energies) of the In 4d, P 2p, As 3d, Ga 3d and C 1s core level emission lines refer to the Fermi edge determined by photoemission from a molybdenum sample holder in electrical contact with the samples. The core level spectra were analyzed by numerical deconvolution into pairs of spin orbit-split doublets each of which consists of convoluted Lorentzian and Gaussian line shapes corresponding to lifetime and experimental broadening, respectively. The measured data points (spheres in Fig. 2-4) are shown together with best-fit from numerical analysis (full lines). For all measurements at the InP samples, a lifetime broadening for the In 4d (P 2p) core levels of 0.1 eV (0.06 eV), a branching ratio of 1.5 (2.0), an experimental broadening of 0.46 eV (0.41 eV), and a spin-orbit splitting of 0.86 eV (0.87 eV) were found. For the measurements at the GaAs samples, a lifetime broadening for the As 3d (Ga 3d) core levels of 0.1 eV (0.1 eV), a branching ratio of 1.5 (1.7), an experimental broadening of 0.50 eV (0.39 eV), and a spin orbit-splitting of 0.69 eV (0.43 eV) were found. The resulting residuum is shown below each fit.

4. Results and Discussion

4.1. *Results for the adsorption of cyclopentene on the InP(001)(2 × 4)*

For the adsorption of cyclopentene on the InP(001)(2 × 4) reconstructed surface, it is well known that the two different surface bonding sites lead to a change for the surface core level components in In 4d and P 2p core levels, as seen in Fig 2. These changes are explained by an adsorption of cyclopentene on the 'mixed-dimer' as the main surface adsorption site. Additionally, subsequently bonding to the second layer *In-In* bonds is observed as we could show in our previous work.²¹

Beside the two surface components in the In 4d core level emission line^{22,23} (shaded) which are revealed by numerical analysis, an additional component after cyclopentene saturation is found. This component shifted towards lower kinetic (higher binding) energies, *In-C*, is assigned to a bond formation of cyclopentene to the topmost In atoms.²¹ For the P 2p core level a second surface related component shifted towards lower kinetic (higher

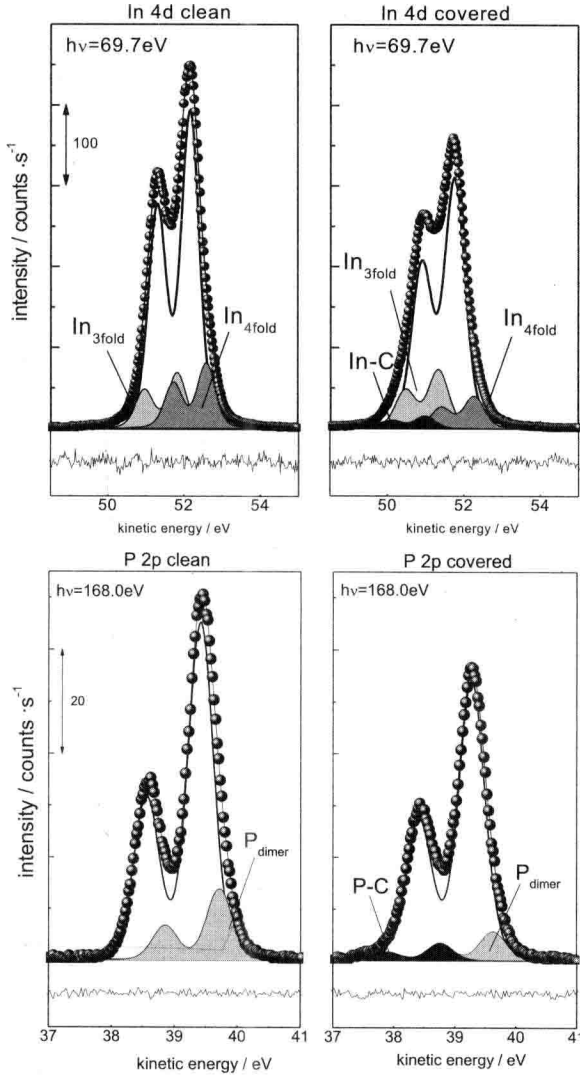


Fig. 2. The In 4d (first row) and P 2p (second row) core level emission lines for the clean (left) and cyclopentene saturated (right) InP(001)(2×4) reconstructed surface from.²¹

binding) energies, $P-C$, is found too. This component is assigned to a bond formation of cyclopentene to the topmost P atoms.²¹

These components are explained to stem from In and P atoms which bond to carbon atoms of the cyclopentene molecules. The shift towards higher binding energies results from a charge transfer from In and P (1.8 and 2.2) to C (2.5) due to the higher electronegativity of the latter.

These observations are supported by the C 1s core level, as shown on the left graph of Fig. 3. Three main components have been revealed by the numerical analysis, $C-C$, $C-In$ and $C-P$, and the energy shifts of the latter components are given with respect to the $C-C$ component. These components are assigned to carbon atoms with $C-C$ single bonds, to carbon atoms involved in a $C-In$ (shift of +1.54 eV) bond and to C atoms involved in a bond formation to P atoms (shifted by +0.50 eV). The shifts in the energy level are in agreement with the different electronegativity values of phosphorus, indium and carbon. The fourth small component is shifted by -1.17 eV towards lower kinetic (higher binding) energies with respect to the $C-C$ component. This component is believed to result from carbon atoms participating in $C=C$ double bonds of cyclopentene as observed by Liu and Hamers.²⁴

These observations are explained by the adsorption of cyclopentene on the 'mixed-dimer' as the main surface adsorption site and subsequently bonding to the second layer $In-In$ bonds as discussed before and are supported by theoretical DFT calculations.²¹

The resulting adsorption structures are based mainly on the analysis of the C 1s core level emission lines. The interpretation and comparison of these results to the ones found for the adsorption of cyclopentene on the GaAs(001)(2×4) surface will help discussing the resulting adsorption structures for the latter.

4.2. Results for the adsorption of cyclopentene on the GaAs(001)(2×4)

The clean (2×4) reconstructed GaAs (001) surface (see Fig. 4 left), two surface related components are found in the emission line shape analysis. One component As_1 is shifted towards lower kinetic (higher binding) energies with respect to the bulk component which is not yet clearly assigned, and another component shifted towards higher kinetic (lower binding) energies are related to the As dimer atoms of the topmost layer of the surface.

In Fig. 4 (middle) the As 3d core level emission line taken after the adsorption of cyclopentene is shown. An additional component ($As-C$) is revealed

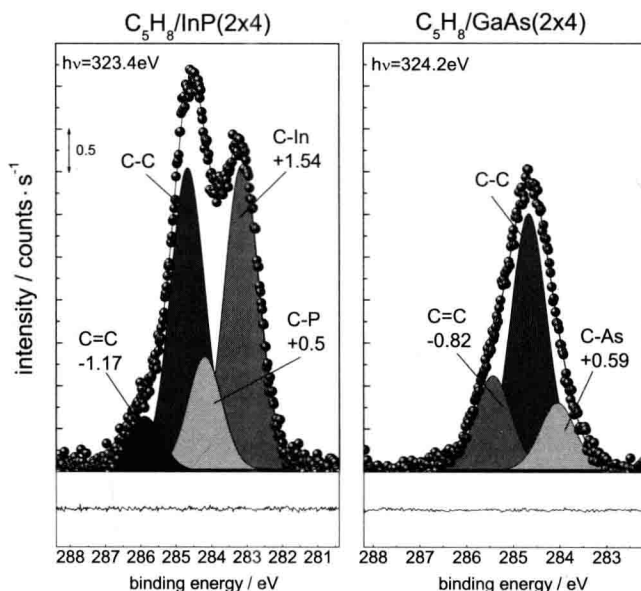


Fig. 3. The C 1s core level for the cyclopentene covered InP(001)(2 × 4) (left) and the cyclopentene covered GaAs(001)(2 × 4) (right) reconstructed surfaces. The shifts are given in eV with respect to the C – C components.

in the fit shifted towards lower kinetic (higher binding) energies. Due to the different electronegativities of C and As (2.5 and 2.2, respectively), this component is assigned to a bond formation between C and As atoms of the topmost layer.

In the Ga 3d core level emission line shape no change could be found after the adsorption of cyclopentene. In Fig. 4 (right) the Ga 3d core level emission line of the cyclopentene covered surface is depicted. Three components are evaluated two of which can not yet clearly be assigned, namely the Ga_1 shifted towards lower kinetic (higher binding) and Ga_2 shifted towards higher kinetic (lower binding) energies. The $Ga_{2ndlayer}$ component, is related to Ga atoms of the second layer.

In Fig. 3 (right side) the C 1s core level emission line taken after the saturation with cyclopentene is shown. Before deposition, no traces of carbon could be detected by SXPS. In the core level line shape analysis three components are found. The first pronounced component is assigned to C atoms