Available online at www.sciencedirect.com

SCIENCE DIRECT®

Surface Science 582 (2005) 90–96

SURFACE SCIENCE

www.elsevier.com/locate/susc

Core level photoemission studies of the interaction of pentacene with the Si(1 1 1) (7 × 7) surface

G. Hughes [a,*], D. Carty [a], A.A. Cafolla [a,b]

[a] *School of Physical Sciences and National Centre for Sensor Research (NCSR), Dublin City University, Ireland*
[b] *Institute for Advanced Material Science (IAMS), Trinity College Dublin, Ireland*

Received 11 January 2005; accepted for publication 24 February 2005

Abstract

The chemical bonding interactions of molecular pentacene with the atomically clean Si(1 1 1) (7 × 7) surface were investigated by high resolution core level and valence photoemission spectroscopy. Thin films of pentacene were deposited from a thermal evaporator onto the atomically clean Si(1 1 1) surface in ultra-high vacuum at room temperature. Analysis of the Si 2p core level spectra reveal evidence of a strong chemical interaction between the first molecular layer and the surface with a chemically shifted component appearing on the lower binding energy side of the Si 2p core level. A 0.30 eV shift of the Si 2p core level towards the valence band maximum indicates that the bonding interaction between the molecules and the surface removes the bandgap states which pin the Fermi level midgap on the clean surface. Valence band spectra reveal that these interactions result in significant changes to the electronic structure of the chemically bonded molecular layer. Subsequent layers display the characteristic molecular orbital spectrum of the pentacene molecule. A reduction in the workfunction can be attribute to the formation of an interface dipole which reaches a maximum of 0.55 eV for a monolayer coverage.
Published by Elsevier B.V.

Keywords: Soft X-ray photoemission; Pentacene; Silicon; Band offsets; Workfunction

---

1. Introduction

Developing an understanding of the interaction of organic thin films with semiconductor surfaces is a prerequisite to the development of hybrid devices combining the flexibility of organic synthesis with the processing power of silicon [1,2]. It is crucial to address issues such as the precise bonding interactions between the first molecular monolayer and the surface as this strongly influences the nucleation and growth of the organic film. The mechanism of layer by layer growth of ultra thin

---

[*] Corresponding author. Tel.: +353 1700 5390; fax: +353 1700 5384.
E-mail address: greg.hughes@dcu.ie (G. Hughes).

0039-6028/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.susc.2005.02.045

pentacene films on atomically clean and organically modified Si(1 0 0) surfaces has recently been investigated [3–5]. These studies have shown that when pentacene is directly deposited onto the clean silicon surface, there is significant chemical interaction between the first organic layer and the surface which disrupts the electronic and physical structure of the molecule. Once this chemically reactive layer, which acts to mediate the strength of the chemical interaction between the reactive surface and the molecular layer has formed, subsequent nucleation of a crystalline film results.

The focus of this paper is to investigate the chemical and structural bonding interactions of thin pentacene layers with the atomically clean Si(1 1 1) surface. Core level photoemission studies reveal details of the changes induced in the chemical bonding environment of the silicon surface atoms following the deposition of molecular pentacene. The photoemission results indicate that there is strong covalent bond formation between the first monolayer and the silicon surface atoms. Valence band studies show that the initial bonding interactions are between the molecule and the rest atoms on the surface. These spectra also show that the electronic structure of the molecules involved in direct bonding interactions differ significantly from molecular layers subsequently absorbed on top of this layer.

2. Experimental

Boron doped silicon ($1–2 \times 10^{16}\,\mathrm{cm}^{-3}$) was resistively heat cleaned in ultra-high vacuum (UHV) until it displayed a (7×7) LEED pattern. Pentacene molecules (Aldrich Chem.) were subsequently deposited at 423 K, without prior purification, for a highly controllable low temperature thermal evaporator onto the clean silicon surface. Soft X-ray photoemission measurements were carried out on the SGM1 monochromator at the ASTRID synchrotron using a SCIENTA SES-200 electron energy analyser. The analyser collects photoelectrons over a solid angle of 8° centred at 40° from the direction of the incoming photons. The SGM monochromator and the SCIENTA analyser were set up such that the combined instrumental resolution was 70 meV for the Si 2p and 200 meV for the C 1s measurements. The core level spectra were curve fitted using a least squares fitting procedure which used Voigt profiles to distinguish between chemically shifted component peaks. The Gaussian line widths were fixed at 90 meV and the Lorentzian widths were fixed at 260 meV for the bulk core peak and 280 meV for the surface components. The spin–orbit splitting was fixed at 603 meV and the branching ratio was 0.5.

Valence band spectra were acquired in both s- and p-polarised orientations. Synchrotron radiation light is polarised in the plane of the storage ring. The sample is mounted perpendicular to the horizontally incident polarised radiation. s- and p-polarised radiation are selected by rotating the sample around the axis along which it is mounted so that the surface is nominally perpendicular to the incident radiation for s-polarised radiation and nominally parallel to the incident radiation for p-polarised radiation.

Geometric constraints of the experimental chamber dictate that in the s-polarised orientation (normal incidence light), the analyser is at 36° off normal and in the p-polarised orientation, the light vector is at 72° with respect to surface normal. This means that while almost exclusively s-polarised spectra can be acquired at 36° off normal, the p-polarised spectra contain a component of s-polarised radiation. The secondary electron cut-off was recorded with the sample biased negatively with respect to the analyser. The energy positions of the low energy cut-off and the highest occupied level were determined by linear extrapolation to the background. The ionisation potential (IP) of the sample was established for each stage of the experiment by subtracting the width of the energy distribution curve from the photon energy.

3. Results

Core level spectra of the clean and pentacene covered Si(1 1 1) surface are presented in Fig. 1. Because of the highly anisotropic shape of the pentacene molecule it is necessary to know the orientation of the molecule on a surface in order to