

The role of π -conjugation in attachment of organic molecules to the silicon (001) surface

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Abstract

We have investigated the role of conjugation in attachment of multifunctional organic molecules to the Si(001) surface. The model molecules we have chosen are acrylonitrile ($\text{CH}_2=\text{CHC}\equiv\text{N}$) and allyl cyanide ($\text{CH}_2=\text{CHCH}_2\text{C}\equiv\text{N}$) due to the electron-withdrawing nature of the cyano group. X-ray photoelectron spectroscopy shows that significant difference in primary binding configuration exists. Infrared spectroscopy establishes that acrylonitrile attaches to the Si(001) surface primarily through a mechanism involving the cyano group, leading to a novel ketenimine structure that is evidenced by characteristic strong infrared absorbance at 1985 cm^{-1} . Allyl cyanide adsorbs in a way that principally utilizes the vinyl portion of the molecule, leading mainly to alkane infrared absorbance below 3000 cm^{-1} . These results show that conjugation can play an important role in controlling product distribution when attaching multifunctional organic molecules to the Si(001) surface.

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Keywords: X-ray photoelectron spectroscopy; Infrared absorption spectroscopy; Chemisorption; Alkenes

1. Introduction

The fabrication of well-defined interfaces between silicon and organic materials has attracted a great deal of attention over the last several years due to emerging applications in new microelectronics technologies [1,2] and for linking microelectronics with biological molecules [3]. While there are many approaches to making organic interfaces to silicon, recent studies have focused on establishing links between the chemistry of silicon surfaces and the chemistry of other compounds known from organic or inorganic chemistry.

The bare Si(001) surface is composed of highly ordered arrays of reactive Si=Si dimers which are analogous to the C=C bonds of alkenes and Si=Si bonds of silenes. However, there are two important differences between surface dimers and alkenes or silenes. The first difference is that the bonds between the Si=Si dimers and the underlying bulk are not planar; thus, the intrinsic hybridization of the surface dimers is somewhere between sp^2 and sp^3 . Secondly, the Si dimers are able to tilt out of the surface plane; this leads to charge transfer between the two atoms and contributes some zwitterionic character to the dimer [4].

One consequence of the unique geometric and electronic structure of Si=Si dimers is that many reactions can occur on the Si(001) surface that would not be facile in analogous solution-phase

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