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Alkyl-terminated Si(111) surfaces: A high-resolution, core level photoelectron spectroscopy study

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The bonding of alkyl monolayers to Si(111) surfaces has been studied with high-resolution core level photoelectron spectroscopy (PES). Two very different wet-chemical methods have been used to prepare the alkyl monolayers: (i) Olefin insertion into the H–Si bond of the H–Si(111) surface, and (ii) replacement of Cl on the Cl–Si(111) surface by an alkyl group from an alkyllithium reagent. In both cases, PES has revealed a C 1*s* component shifted to lower binding energy and a Si 2*p* component shifted to higher binding energy. Both components are attributed to the presence of a C–Si bond at the interface. Along with photoelectron diffraction data [Appl. Phys. Lett. **71**, 1056, (1997)], these data are used to show that these two synthetic methods can be used to functionalize the Si(111) surface. [S0021-8979(98)00324-7]

I. INTRODUCTION

The placement of organic functional groups on semiconductor surfaces is of great interest in gas and biochemical sensor development and in the semiconductor industry as passivation layers where an oxide film cannot be used. Recent studies reporting on the modification of silicon surfaces using Langmuir–Blodgett (LB) techniques[1–5] have shown possible applications as biosensors[4] and as field effect transistors.[5] Unfortunately, the organic thin films made using LB techniques often have an oxide layer at the interface which can influence device characteristics. In this article, we will show that a monolayer of an organic functional group can be directly attached to Si(111) surfaces without the need of LB techniques and thus without an intervening oxide layer by using the methodology developed by Linford and Chidsey[6–8] where (i) olefin insertion into the H–Si bond of the H–Si(111) surface, or (ii) replacement of Cl on the Cl–Si(111) surface by an alkyl group from an alkyllithium reagent is used to form a direct C–Si bond.

Preliminary evidence of monolayer formation had been gained from infrared absorption spectroscopy, low-resolution x-ray photoelectron spectroscopy, ellipsometry, x-ray reflectivity, and contact angle measurements.[6,7] These preliminary studies had indicated that the monolayers are extraordinarily stable in atmosphere and under harsh conditions such as boiling solvents and boiling aqueous acids, but had provided no direct evidence of surface bonding. In this work, high-resolution core level photoelectron spectroscopy was used to determine the electronic structure of the interface of samples prepared using the methods outlined above. Core level photoemission spectra[9] have been shown to be very sensitive to the local chemical environment of the emitting atom. The C 1*s* and Si 2*p* photoemission spectra from these samples were decomposed into two components. In both cases, it was possible to assign a component to bulk-like emission from silicon atoms deep in the crystal (Si 2*p* spectra) or to carbon atoms in the alkyl chain (C 1*s* spectra). The other component was then attributed to emission from the C or Si atoms at the interface between the alkyl monolayer and the silicon crystal. The presence of these interfacial components strongly suggests that strong chemical bonding occurred between the alkyl group and the silicon surface.

The alkyl monolayers were annealed to various incremental temperatures, and after the samples cooled to room temperature, photoemission spectra were collected. Evidence of silicon–carbon alloying was observed. The alloy disappeared when the annealing temperature reached 700 °C. Therefore, the alkyl chains may be useful as a carbon source in silicon carbide thin film growth or by providing sp^3 hybridized C nucleation sites for diamond growth.

The results of this work show that densely packed monolayers of alkyl groups, $H_{2n+1}C_n$, with chain lengths (n) of 1 to 18, on Si(111) surfaces with no intervening oxide have been prepared using the methods of Linford and Chidsey.[6–8]

II. EXPERIMENT

A. Sample preparation and transportation

Steps 1 and 2 of the preparation of the alkyl-terminated Si(111) surfaces involved the growth of a thin silicon oxide film; followed by the removal of this film. This procedure was first described by Higashi, and co-workers.[10] This preparation was chosen because the resultant surface has been shown to have a low step density along with large, uniform terraces, i.e., a nearly ideal starting surface for chemical synthesis. The oxide film was grown using the following

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