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Formation of covalent Si–N linkages on pyrrole functionalized Si(100)-(2 × 1)

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Abstract

The covalent attachment of a pyrrolyl monolayer has been efficiently achieved by directly exposing pyrrole molecules to the clean Si(100)-(2 × 1) surface. The high-resolution electron energy loss spectroscopy (HREELS), and X-ray photoelectron spectroscopy (XPS) studies show that the robust pyrrolyl monolayer is directly bonded to the Si(100) surface via the Si–N linkage with the preservation of the pyrrolyl ring structure. The as-prepared pyrrole-modified silicon surfaces can serve as templates for further electrochemical polymerization of polypyrrole thin films onto silicon substrates, providing new opportunity for fabrication of new polypyrrole/silicon heterojunctions with improved performance. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, the use of conducting polymer thin films as active components in various microelectronic applications has attracted increased attention [1,2]. Compared to conventional inorganic devices, the conducting polymers offer unique combinations of electrical, mechanical and physical properties in the fabrication of composite devices [3]. Furthermore, the chemical modification provides additional opportunities for fine-tailoring the important electrical properties. Of all conducting polymers, polypyrrole is most attractive due to its high conductivity and interesting mechanical properties [4]. In particu-

lar, it is considered to be the promising candidate for the fabrication of various current-control composite devices. For instance, electropolymerized polypyrrole thin films on either p-type silicon [5] or n-type InP [6] have recently been investigated for their potential use as Schottky diodes. However, the adhesion between the polymer and semiconductor obtained from electro-polymerization is quite poor due to the weak physical interaction [7]. As a result, the stability and performance of most of the composite devices are still much lower than that of the conventional inorganic devices. For practical device applications, high-quality junctions with good adhesion between the polymer/semiconductor are essentially required.

To enhance the binding between polypyrrole thin film and semiconductors, various surface modification strategies employing wet-chemistry methods

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have been reported [8], where functionalised pyrroles assembled on semiconductor substrates were widely used as templates or 'molecular glues' for subsequent polymerization of thin films onto semiconductors. For instance, conducting polypyrrole thin films have been prepared by chemical polymerization on a silane-bearing pyrrole modified SiO_2–Si surface by Wu et al. [9], and a high conductivity up to 1.6 $S \cdot cm^{-1}$ was achieved. More recently, the pre-modification of surfaces by reacting pyrrole-terminated alkyllithium reagents with hydrogen passivated silicon surfaces was shown to greatly improve the electrical properties in device performance tests [10]. However, the use of organolithium reagents may not be compatible with some semiconductor processes where metal contamination of the surface should be avoided.

In the present work, we report for the first time the covalent attachment of pyrrole molecules onto the silicon substrates. High-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) have been employed to investigate the structure and thermal stability of the pyrrole assembly on the Si(100) surfaces. Our results show that the ordered pyrrolyl-assembly is covalently bonded to the silicon substrates via a Si–N linkage. The aromatic ring structure is retained in the robust pyrrole/Si assembly (Scheme 1), allowing the further formation of polypyrrole thin films on the pyrrole modified silicon surfaces. This capability can lead to the development of new polypyrrole/semiconductor heterojunctions with improved performance.

2. Experiment

The experiments were carried out in stainless-steel UHV systems [11,12] equipped with HREELS (LK-2000), XPS (VG Microtech), and a mass spectrometer (UTI-100). The base pressure of the UHV chambers was maintained below 2×10^{-10} Torr. An n-type (P-doped) silicon wafer (1–30 $\Omega \cdot cm$) with a size of $16 \times 8 \times 0.38$ mm^3 was used as the substrate. The clean Si(100)-(2×1) substrate was prepared by cycles of Ar$^+$ bombardment (2.0 KV, 30 min) and subsequent annealing to 1300 K. The cleanliness of Si(100)-(2×1) was confirmed by the absence of adsorbate-related features in XPS and HREELS. Prior to surface reaction, pyrrole (98%, Aldrich) was further purified by several freeze–pump–thaw cycles. The HREEL spectra were recorded with a primary electron beam energy (E_p) of 6.0 eV in a specular scattering geometry ($\theta_i = \theta_s = 60°$). The XPS spectra were acquired using Al Kα radiation ($h\nu = 1486.6$ eV) from an anode source (VG) operated at 300 W [12]. Photoelectrons were detected by a concentric hemispherical analyser (CHA, VG100) with a 20 eV pass energy. The binding energy (BE) scale was referenced to the substrate Si$_{2p}$ peak at BE of 99.3 eV.

3. Results and discussion

Fig. 1 shows the vibrational spectra obtained after annealing the pyrrole-exposed (4.0 L, 1 L = 10^{-6} Torr $\cdot$ s) silicon surface to various temperatures. Upon adsorption at 300 K, the absence of the N–H stretch
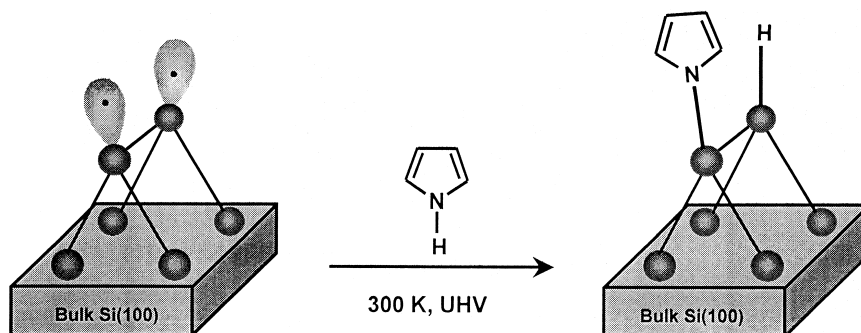
Scheme 1. A schematic model for covalent attachment of a pyrrolyl group via the Si-N linkage onto one silicon atom of a Si=Si dimer on Si(100)-(2×1). Note that the dissociated hydrogen atom is bonded to the neighboring silicon atom in the same dimer.
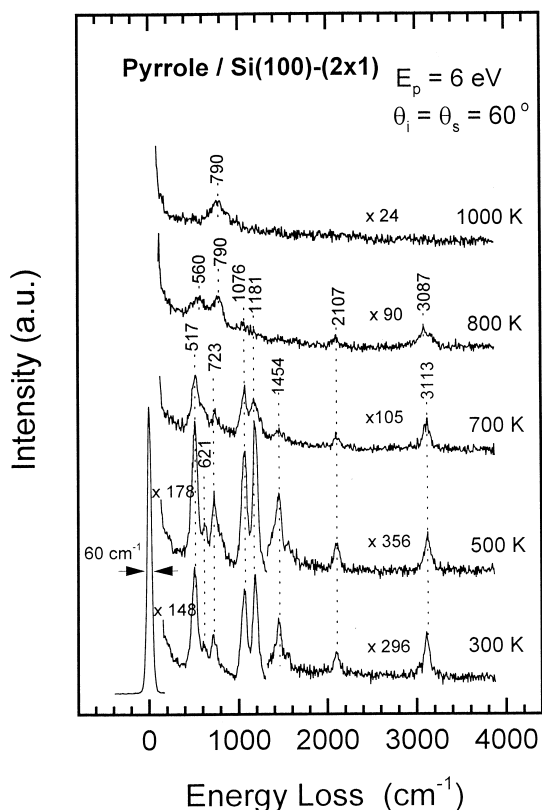
Fig. 1. HREELS spectra for pyrrole (4.0 L) assembly on Si(100)-(2×1) at room temperature and the surfaces annealed at indicated temperatures.

at 3400 cm^{-1} [13] and the observation of the Si–N stretch at 517 cm^{-1} [14] together with the XPS results (see below) indicate that pyrrole reacts with Si(100)-(2 × 1) through the cleavage of the H–N group, forming a Si–N linkage between the substrate and the pyrrolyl ring (Scheme 1). Meanwhile, the appearance of the vibrational loss at 2107 cm^{-1} corresponding to Si–H stretch mode [14] demonstrates the binding of the dissociated hydrogen atom to one of the neighboring dangling Si bonds. The presence of vibrational features at 1454, 1181, 1076 and 723 cm^{-1} clearly shows that the pyrrolyl ring remains intact upon chemisorption [13]. The peaks at 1454 and 723 cm^{-1} can be attributed to ring stretch/deformation and C–H out-of-plane bending modes, respectively. The loss features at 1181 and 1076 cm^{-1} are related to the C–H in-plane bending modes [13]. The observation of the intense features

corresponding to the C–H in-plane bending modes suggests that the chemisorbed pyrrolyl ring stands almost upright on the substrate surfaces. In addition, the loss features corresponding to the C–H stretch (3113 cm^{-1}) [13] and Si–H bending (621 cm^{-1}) [15] modes are also resolved. In the thermal desorption experiments, only H$_2$ ($m/e = 2$) and HCN ($m/e = 27$) were detected around 850 K. The absence of molecular desorption ($m/e = 67$, C$_4$H$_5$N$^+$) excludes the formation of pyrrole multilayers on silicon substrates at room temperature under UHV conditions.

Annealing the pyrrole assembled silicon surfaces to 500 K leads to a significant enhancement of the EELS elastic beam intensity, indicative of the formation of a highly ordered pyrrolyl monolayer. However, the characteristic aromatic ring structures are still retained even at 700 K. This observation displays the remarkable thermal stability of the pyrrole assembly on Si(100)-(2 × 1). Subsequent annealing to temperatures above 800 K gives broad features around 790 cm^{-1}, associated with Si–carbide or Si–nitride species due to the complete decomposition of the Si–N linked pyrrolyl groups on silicon surfaces [16].

The structure and thermal stability of the surface assembly are further investigated with XPS. Fig. 2 presents the C1s and N1s spectra for the pyrrole-assembled silicon surfaces annealed to different temperatures. At 300 K, the BE of the N1s peak is located at 399.3 eV, much lower than the value of 400.4 eV corresponding to the pyrrole condensed at 110 K on the same surface [1]. In contrast, the BE of C1s in the pyrrole assembly is 284.4 eV, shifting only slightly from the C1s value of 284.8 eV for the physisorbed pyrrole molecules (see footnote 1). This observation provides strong support for the proposed model based on the HREELS results, in which the pyrrolyl group is attached to the surface via the Si–N linkage. Based on the XPS peak area analysis, the relative surface coverage of the pyrrolyl groups is determined to be ~ 0.46 ML (molecule to surface Si

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[1] For comparative purposes, the HREELS and XPS experiments were also conducted at temperatures well below 300 K. Our results show that only the physisorbed multilayer pyrrole was present on Si(100)-(2×1) upon pyrrole adsorption at 110 K.
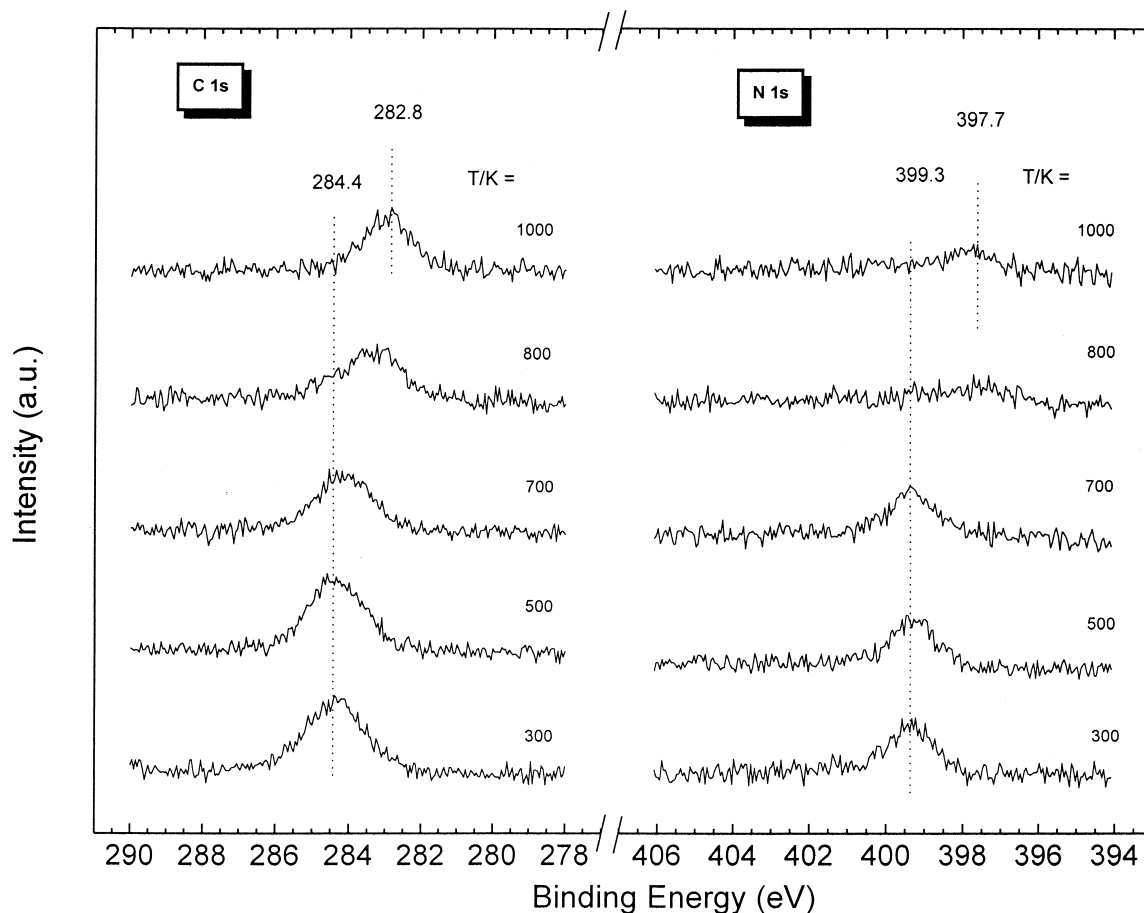
Fig. 2. XP spectra of C1s and N1s core levels for pyrrole (4.0 L) assembled on Si(100)-(2 × 1) annealed at the indicated temperatures.

atom ratio), corresponding to each molecule attached to one silicon dimer, as illustrated in Scheme 1.

Upon annealing, the peak positions and intensities for both N1s and C1s regions remain identical from 300 to 700 K, suggesting no significant chemical changes occurring in this temperature range. However, both the peak position and intensity of N1s change significantly upon progressive annealing at above 800 K; for C1s, only a large shift in peak position is observed. This observation suggests the further decomposition of the pyrrole assembly on silicon surfaces occurs upon annealing at above 800 K. The N1s binding energy of 397.7 eV, obtained after annealing at 1000 K, is close to that of nitride species (396 ∼ 398 eV; 397.4 eV for bulk silicon nitride) [17], while C1s BE shifts to 283 eV,

typical for carbides [18]. This result clearly suggests the complete decomposition of the carbon-containing pyrrolyl ring and subsequent formation of the silicon carbide and nitride on the surface.

Our results demonstrate a novel approach for facile and efficient attachment of a robust pyrrole monolayer through the covalent Si–N linkage beyond those based on the Si–C linkage to the silicon surfaces. Although the pyrrole molecule possesses the C=C–C=C group that may lead to the di-σ attachment of the pyrrole molecule to the Si(100) surface with the formation of Si–C bonds through a cycloaddition reaction [19–21], our experiments show that the N–H cleavage reaction operates in the present pyrrole/Si system. The unexpected N–H cleavage reaction results in the subsequent covalent bond-

ing of pyrroyl species and the corresponding H atoms to the reactive silicon dangling bonds, leading to the direct attachment of the pyrrolyl ring group to the silicon surface via a Si–N linkage. Our approach is different from previous assembly reactions of amine molecules on a silicon surface using the Si–N linkage reported by Bergerson et al. [18], where the covalent attachment was achieved by the reaction of the –NH$_2$ group in amines with the pre-chlorinated Si(100) surface.

4. Summary

In summary, our results show clearly that a robust pyrrole monolayer with the Si–N linkage can be efficiently achieved by vapour deposition of pyrrole molecules to the clean Si(100) surface in UHV. The present approach is clean and facile. The pyrrolyl species in the organic monolayer stand nearly vertical on the silicon substrate, and preserve the aromatic ring structure. In addition, the as-prepared organic monolayer displays a high thermal stability upon annealing. The pyrrole monolayer directly extending from the silicon lattice can be used as a promising 'molecular glue' or a template for development of electrochemically derived polypyrrole/silicon heterojunctions with intimate contact between the two phases.

Acknowledgements

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