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High-resolution photoemission studies of the interfacial reactivity and interfacial energetics of Au and Cu Schottky barriers on methyl-terminated Si(1 1 1) surfaces

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Abstract

The Schottky junction formation by the stepwise evaporation of gold and copper, respectively, onto methyl-terminated silicon, CH_3–Si(1 1 1), was investigated by synchrotron X-ray photoelectron spectroscopy. During the junction formation process, interface reactions occurred as revealed by the appearance of chemically shifted Si 2p components. Upon deposition of Au, the formation of about one monolayer of gold silicide, $SiAu_3$, with a Si 2p chemical shift of +0.75(2) eV, was observed. The $SiAu_3$ floated on top of the growing gold layer. Similarly, for the deposition of Cu, the methyl termination layer was partially disrupted, as indicated by the appearance of a −0.28(2) eV chemically shifted Si 2p component attributable to an interfacial copper silicide phase, $SiCu_3$. Hence, the termination of the Si(1 1 1) surface by methyl groups did not completely prevent interfacial reactions, but did reduce the amount interfacial reaction products as compared to bare Si(1 1 1)-(7 × 7) surfaces.

Electron Schottky barrier heights of 0.78(8) eV (Au) and 0.61(8) eV (Cu) were measured. Within the experimental uncertainty the observed Schottky barriers were identical to those ones obtained on non-passivated, (7 × 7)-reconstructed Si(1 1 1) surfaces. Thus, the modification of the electronic properties of the silicon–metal contact requires the complete absence of interfacial reactions.

Keywords: Synchrotron radiation photoelectron spectroscopy; Silicon; Copper; Gold; Metal–semiconductor interfaces; Schottky barrier; Alkanes; Silicides

1. Introduction

Alkylation of Si(1 1 1) surfaces has been widely explored for its ability to impart molecular level control over the chemical and electrical properties of Si surfaces. Alkyl groups have been introduced through direct Si–C bonds using UV or thermally catalyzed olefin addition [1–4], electrochemical polarization, or reaction of the Cl-terminated Si surface with organic Grignard or Li reagents [5–12], amongst other methods. Methyl groups are the only saturated alkyl group that sterically can terminate every Si atop site on an unreconstructed Si(1 1 1) surface [13], hence CH_3–Si(1 1 1) surfaces are especially interesting. The CH_3–Si(1 1 1) surface, as well as other alkylated Si surfaces, can be prepared by a two-step chlorination/alkylation method [5,14]. Alklyation has been shown to improve the resistance to chemical and electrochemical oxidation of Si relative to the H-terminated Si(1 1 1) surface [6,8,14,15], to provide a low density of electrically active surface states [11,12,14,15], and to modify the surface dipole relative to that at H–Si(1 1 1) surfaces [12].

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Fermi-level pinning and metal silicide formation are both commonly observed on Si(1 1 1)–metal Schottky barriers. A question of interest is the extent to which modification of the Si surface with a $-CH_3$ group can effect a modification in the electrical and chemical properties of such Si–metal Schottky barriers. Hence, in this work, we report studies of the energetics and interfacial chemistry of CH_3–Si(1 1 1) surfaces onto which Schottky barrier contacts have been formed with Au and Cu. Au and Cu have different work functions but are well-known to be reactive with Si [16–24]. Studies of these contacts therefore ought to provide information on whether Fermi-level pinning can be controlled by introduction of $-CH_3$ groups onto the Si surface. The reactivity and energetics of the interfaces have been probed using high-resolution synchrotron photoemission methods, which provides information on the chemical state of the interface as well as on the electrical properties, including the band bending, interfacial dipole, and barrier heights, of the Si–metal contacts of interest.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Silicon(1 1 1) wafers polished on one side to a thickness of 380 μm with a miscut angle of ±0.5° were obtained from ITME (Poland). These n-type samples were doped with Sb to a resistivity of 0.005–0.02 Ω cm. This doping level corresponds to a Fermi level position in the bulk of the wafers of 1.04(2) eV above the valence band maximum, E_v.

All solvents used in alkylation reactions were anhydrous, stored under $N_2(g)$, and used as received from Aldrich Chemical Corp. Solvents were only exposed to the atmosphere of a $N_2(g)$-purged flush box. Water with a resistivity >18.0 MΩ cm was used at all times. All other chemicals were used as received.

2.1.2. Sample preparation

Before chemical functionalization, each sample was cleaned by rinsing in a flowing stream of H_2O, CH_3OH, acetone, CH_3OH, and H_2O, respectively. After cleaning, the sample was placed directly in 11 M (i.e., 40% by weight) $NH_4F(aq)$ (Transene, Inc.) for 20 min to etch the native oxide layer and produce a H-terminated Si(1 1 1) surface. During the etching process, the wafers were agitated occasionally to remove the bubbles that formed on the surface. After removal from the etching solution, the sample was rinsed thoroughly with H_2O and dried under a stream of $N_2(g)$. The sample was then placed into the antechamber of a $N_2(g)$-purged glove-box for further chemical functionalization.

Hydrogen-terminated Si(1 1 1) surfaces were chlorinated according to previously published procedures. A freshly etched surface was first immersed in a saturated solution of PCl_5 (99.998%, Alfa Aesar) in chlorobenzene to which a few grains of benzoyl peroxide had been added. The reaction solution was then heated to 90–100 °C for 45 min. The sample was then removed from the reaction solution, rinsed with tetrahydrofuran (THF) and CH_3OH, and dried with a stream of $N_2(g)$.

For alkylation, the Cl-terminated Si(1 1 1) sample was immersed in a 3 M solution of CH_3MgBr in THF (Aldrich). Excess THF was added to each reaction solution to allow for solvent loss. The reaction solution was heated to 70–80 °C for 5 h. At the end of the reaction, the sample was removed from the solution and rinsed with copious amounts of THF and CH_3OH, then immersed in CH_3OH and removed from the N_2-purged glove-box. The sample was sonicated for 5 min in CH_3OH, sonicated in CH_3CN for a further 5 min, and then dried under a stream of $N_2(g)$. Sonication was required for complete removal of adsorbed Mg salts from the surface of the sample. The CH_3-terminated Si(1 1 1) samples were then sealed under $N_2(g)$ and transported to the BESSY synchrotron facility in Berlin. Samples were received in <2 days from the time of preparation, and then stored in an Ar-purged glove-box with H_2O and O_2 concentrations of $\leqslant$ 1 ppm for 10 further days.[1] The samples were then mounted onto OMICRON®-type sample holders and introduced into the vacuum system.

2.2. Metal deposition

Gold and copper were deposited by physical vapor deposition in an ultra-high vacuum deposition chamber that was equipped with direct vacuum transfer to the analysis system [25]. Gold was deposited using a water-cooled effusion cell, whereas Cu was evaporated using a home-made Knudsen cell. Prior to the metal deposition the samples were vacuum annealed for 20 min at ≈390 °C to desorb any adventitious, weakly bound non-methyl hydrocarbon contamination [12]. During depositions, the CH_3–Si(1 1 1) substrates were not heated and were thus nominally at room temperature (not accounting for adventitious heating of the sample due to heat radiated from the hot crucibles during deposition). The deposition experiments were conducted at cell temperatures of 1250 °C for Au and 1130 °C for Cu. The deposition rate of copper was 2.8 Å min^{-1}, as measured prior to the experiments by a quartz crystal flux monitor. The deposition rate of gold was estimated as 0.57 Å min^{-1} by measurement of the attenuation of the Si 2p signal produced by the first, submonolayer, deposition steps. The thickness of a monolayer (ML) of deposited material was 2.6 Å (Au) or 2.3 Å (Cu), as calculated from the bulk parameters for the metal

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[1] During glove-box storage for up to 2 weeks, no significant deterioration of the methylated silicon surface was observed in terms of oxidation or hydrocarbon contamination. The excellent chemical stability of Si(1 1 1)–CH_3 is also evidenced by the substantial inhibition of oxidation in ambient air in comparison to the hydrogen-passivated Si(1 1 1)–H surface (Ref. [14]).