Photoemission study of Au, Ge, and O_2 deposition on NH_4F etched Si(111)

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We have studied the interaction of a metal Au, a semiconductor Ge, and a nonmetal O_2, with the NH_4F etched Si(111) surface with photoemission spectroscopy. Two components were present in Si $2p$ core-level spectra from the H-terminated surface. We observed the flatband condition from the as-etched, n-type, Si(111) surface. We performed stepwise depositions of Au and measured the band bending with photoemission spectroscopy. The Fermi level pinned near midgap as Au was deposited onto the as-etched surface. After the deposition of 1 ML of Au, a Au-silicide layer formed. This interfacial component indicated that the passivating H layer was compromised. As the Au coverage was increased, layers of pure Au formed between the bulk silicon and the Au-silicide layer. The observed behavior was nearly identical to that of Au deposition on the Si(111) 7×7 surface [Phys. Rev. Lett. **67**, 2187 (1991)]. Next, we tested the ability of the monohydride layer to sustain surfactant assisted growth of Ge. Ge islanding was observed at 400 °C indicating that good surfactant growth was not obtained. This was consistent with the recent results of Sakai and Tatsumi [Appl. Phys. Lett. **61**, 52 (1994)] who reported that the surface roughness was nearly the same for surfaces grown with or without H at this temperature. Although the monohydride layer was not a good surfactant for the Si(111) surface at this temperature, further study at different temperatures is needed to determine the ability of the ideal monohydride layer to act as a surfactant. Finally, we observed no oxidation of the as-etched surface at room temperature upon exposure to molecular oxygen.

I. INTRODUCTION

A standard method for preparing silicon surfaces has used HF etching to remove native oxide layers and to protect the surface from chemical attack. However, surfaces prepared in this manner are atomically rough. Due to the surface roughness, mono-, di-, and trihydride species are present.[1,2] Recently, a method for preparing ideal H-terminated Si(111) surfaces by chemically etching in aqueous NH_4F solutions was developed.[1,2] Infrared spectroscopy has shown this surface to be terminated entirely by the monohydride and to be flat on an atomic scale.[1,2] A high-resolution photoemission study of this surface showed that the Si $2p$ core level was very narrow, with a total linewidth of 0.160 eV, and that narrow features related to Si–H existed in the valence band.[3] These features in the core-level and valence-band spectra were much narrower than those previously reported for H–Si(111) prepared by H exposure in vacuum.[4] The discovery of this ideal H-terminated surface has opened up many possible avenues of study.

One area of study involves the interaction of metals with the passivated surface. Recent results of Hg deposition on this H-passivated surface have shown that the Hg/H–Si(111) interface behaves as an ideal Schottky diode.[5,6] The explanation offered for this behavior has the H termination layer remaining between the Hg and Si. In this position, H removes interface states responsible for the nonideality of Schottky barrier heights. If Hg does not displace H, then it follows that H has the ability to prevent certain surface reactions. However, Wittmer and Freeouf[5,6] did not have a probe of surface reactions available to determine if a surface reaction occurred at the interface. They could only measure barrier height and so could not directly determine if Hg displaced H. Photoemission spectroscopy is an ideal probe of surface reactions and of the initial stage of Schottky barrier formation. We applied photoemission spectroscopy to investigate NH_4F etched surfaces that had been exposed to either a metal Au, a semiconductor Ge, or a nonmetal O_2.

II. EXPERIMENT

The experiments were performed with the 6 m toroidal grating monochromator on Beam Line I-2 at the Stanford Synchrotron Radiation Laboratory. The experimental chamber was equipped with a VG ADES 400 angle-resolved hemispherical analyzer with a combined resolution (analyzer and monochromator) of 0.37 eV at a photon energy of 130 eV. We used n-type, Si wafers that were cut in a (111) orientation with less than 1° miscut. These wafers were etched in a 40% solution of NH_4F by weight to produce the ideal H-terminated surface. After etching, the surface was rinsed for 10 s in de-ionized H_2O to remove residual compounds from the etching process. The samples were then introduced into the analysis chamber through our transfer system.

In this study, all depositions were performed at room temperature. Au and Ge were evaporated from tungsten filament evaporators. The depositions were monitored with a quartz-crystal monitor that allowed us to determine coverages to an accuracy of 20%. O_2 was introduced by backfilling the chamber to the designated pressure as measured with an ion gauge. O_2 exposures were measured in langmuirs. After O_2 exposure the chamber was reevacuated to the base pressure of 1×10^{-10} Torr before any measurements were performed.

An electron beam heater was used to anneal the sample. The sample was slowly brought up to the desired temperature to minimize contamination from the sample holder