Atomic-scale Structure of the Ba/Si(001) – (2 × 1) Surface: X-ray Standing Wave Analysis

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Introduction

Submonolayer (sub-ML) surface phases of alkaline earth metals on Si(001) have been of interest recently due to their role as a precursor to the growth of high-quality perovskite films, such as $SrTiO_3$ and $BaTiO_3$, on Si. A (2×1) Ba/Si(001) phase has been reported for Ba coverages ranging from 1/4 to 3/4 ML. There have been conflicting reports over the saturation coverage and atomic-scale structure of this phase [1-4]. In the present work, we use x-ray standing wave (XSW) measurements of a sub-ML (2×1) Ba/Si(001) surface to determine the position of Ba atoms relative to the underlying bulk Si lattice.

Methods and Materials

Experiments were conducted at BESSRC undulator beamline station 12-ID-D at the APS. Molecular beam epitaxy sample preparation, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and XSW measurements were performed in an ultrahigh vacuum (UHV) system with a base pressure of $\sim 1.5 \times 10^{-10}$ torr.

Single-crystal Si(001) samples were treated with a modified Shiraki etch and mounted in a strain-free manner onto molybdenum sample holders prior to introduction into the UHV system. After degassing for ~12 hours at 400-600°C, the samples were annealed for 15 minutes at 850-900°C to remove the chemically grown SiO_2 film and produce a sharp, two-domain (2×1) LEED pattern, indicating a dimerized Si(001) surface. AES showed C and O contamination levels to be less than 0.02 ML (1 ML = 6.78×10^{14} atoms/cm^2).

An effusion cell was used to deposit ~1.3 ML Ba at a rate of 0.02 ML/min onto the room-temperature Si(001) substrates. Subsequent annealing for 5 minutes at 850°C caused the Ba coverage to decrease to 0.31 ±0.03 ML and resulted in a sharp (2×1) LEED pattern. The Ba coverage was determined in UHV by comparing the intensity of the Ba Lα fluorescence from the samples to that of a Ba-implanted Si(001) standard calibrated by Rutherford backscattering spectroscopy (RBS). *Ex situ* RBS was also used to measure the Ba coverage after completion of the XSW experiment. The sample temperature was monitored by using an optical pyrometer and a thermocouple mounted on the sample stage.

Using an incident photon energy of 8.0 keV, UHV XSW measurements of the (2×1) Ba/Si(001) surface were performed by scanning the sample in angles through the silicone (004) and (022) Bragg conditions. The incident beam from the undulator was filtered by a high-heat-load Si(111) monochromator followed by a postmonochromator consisting of a pair of detuned, nondispersive, Si channel-cut crystals. The d-spacing of the postmonochromator matched that of the sample. During each scan, the diffracted beam intensity was monitored with a photodiode, and the x-ray fluorescence spectra were collected by a Si(Li) solid-state detector. The Ba coherent fractions f_H and coherent positions P_H were determined by fitting the reflectivity and normalized Ba Lα fluorescence yield data to dynamical diffraction theory, as described in Refs. 5 and 6.

Results

Experimental data and theoretical fits for the silicone (004) and (022) XSW measurements are shown in Fig. 1. The measured P_{004} = 0.99 corresponds to ordered Ba adatoms located at a height just 0.01 Å below a bulk-extrapolated Si(004) atomic plane (note that this height difference is on the same order as the experimental error). The measured P_{022} = 0.55 is in general agreement with the relationship $P_{022} = P_{004}/2$, a geometrical symmetry requirement for the occupation of cave or bridge sites on the Si(001) surface.

Discussion

While several atomic-scale models of the (2×1) Ba/Si(001) surface have been proposed [1, 3], only that suggested in Ref. 4 and depicted in Fig. 2 is consistent with our results. This model contains Ba atoms occupying cave sites on a dimerized Si(001) surface and saturates the surface at a coverage of 1/2 ML. Our observation of the (2×1) phase at a Ba coverage of just 0.31 ML and the rather modest f_H values, indicating that ~1/2 of the Ba coverage is disordered could be explained by a (2×1) phase (with a *local* coverage of 1/2 ML) covering only a fraction of the surface. These findings, however, could

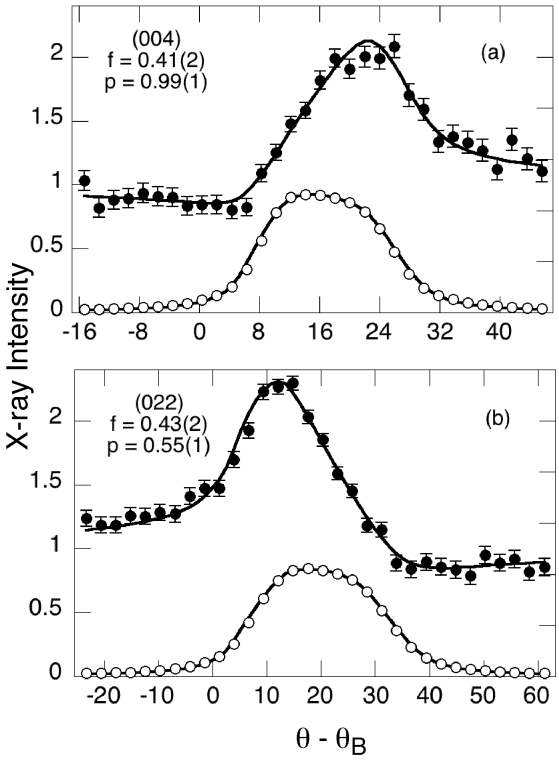

FIG. 1. Reflectivity (open circles) and normalized Ba Lα fluorescence yield (solid circles) experimental data, along with corresponding theoretical fits for the (a) Si(004) and (b) Si(022) XSW measurements.

also be due to the (2×1) phase exhibiting a saturation coverage less than that shown in Fig. 2, and they illustrate the importance of distinguishing between the ordered and disordered fraction of adatoms when mapping out a surface-phase diagram.

Acknowledgments

This work was supported by the National Science Foundation under Contract Nos. DMR-9973436, DMR-0076097, and CHE-9810378. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38 with ANL and DEFG02-03ER15457 with NU. The authors thank the BESSRC staff for technical assistance. We also gratefully acknowledge L. Funk and P. Baldo of ANL for providing the Ba-implanted standard and performing RBS measurements used for coverage determination.

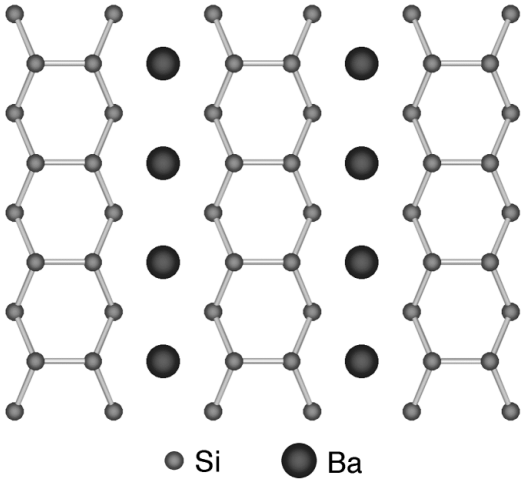

FIG. 2. 1/2 ML (2×1) Ba/Si(001) surface model initially proposed in Ref. 4.

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