

An atomic monolayer of Ag on the Si(111) surface

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Probing an atomic monolayer of 10^{13} atoms adsorbed on an ultra-clean, 600°C, semiconductor surface in ultra-high vacuum with 3.5 to 27 keV x-rays could be an experimentalist's nightmare — if it weren't for the facilities available at CHESS. The initiative to use synchrotron x-rays to study surface structure was launched at CHESS in the 1980's by Professors Bob Batterman, CHESS, and Jack Blakely, Materials Science, with funding provided through Cornell's Materials Science Center. Recently, interesting studies of submonolayers of Ag (adsorbate) on the Si(111) surface have been completed using the X-ray Standing Wave (XSW) and polarization dependent Surface EXAFS (SEXAFS) techniques.

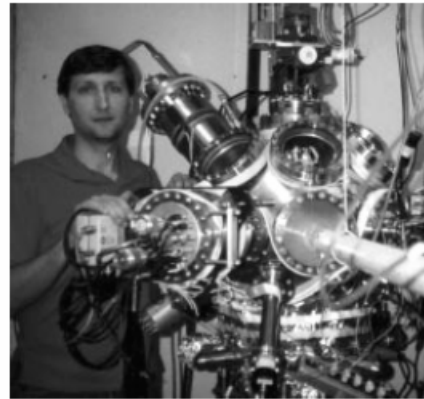
Why Ag? An Enigmatic 2D Phase System.

In 1967, K. Spiegel¹ was probably pragmatically motivated to put silver atoms on a silicon surface. There was a lot to understand about the nature of ohmic and Schottky interfaces at that time. A simple model system was needed where atomic structure was known so that electronic structure

could be calculated. There is only one d-metal/silicon system without a complicating silicide structure; only one combination that bulk studies had unambiguously shown not to intermix — that was the Ag on Si system. Spiegel conducted the first Low Energy Electron Diffraction (LEED) studies and showed that it took 1/3 of a monolayer (1 Ag atom for every 3 Si atoms in the surface unit cell) to cover the surface before subsequent

Ag deposits produced crystalline Ag islands on top of this adlayer. The Ag/Si(111) interface was thus modeled as Ag atoms sitting in hollows formed by three Si surface atoms and making a centered-hexagonal network on the surface (see figure 1).

Today, 27 years later, this simple, non-silicide forming, non-intermixing system of silver atoms on a Si(111) surface has been repeatedly tested, by every available surface science technique. The result — not confirmation or refinement of the original findings — but total chaos! Over 125 different papers from almost as many research groups battle over which of at least fourteen surface structural models their results support. There is no consensus as to how many Ag atoms per Si surface unit cell constitutes a single monolayer and no consensus even as to whether

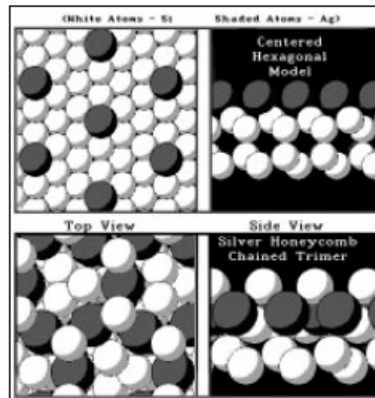


Gary Navrotski with UHV chamber at D-line.

er the Ag atom sits on the Si surface or embeds itself in the top surface layer!

The most famous example of this confusion came in a 1987 *Physical Review Letters*. Two groups, working independently and using the newly developed Scanning Tunneling Microscope (STM) studied the Ag/Si(111) surface. Both groups were members of IBM's research laboratory system; Wilson² at IBM Almaden in California and Van Loenen³ at IBM Watson Research Center in New York. The Almaden group determined that the Ag atoms sat in a honeycomb structure on the Si(111) surface — the Watson group concluded that the Ag atoms were embedded under a Si surface layer.

Today, the theoretical interest in Ag/Si(111) as a model system has long been forgotten. The applied interest in understanding Ag/Si as a Schottky barrier has been supplanted by experience. To surface scientists, Ag on Si(111) has just become an enigma. With the solution of its structure, we can, hopefully, begin to understand the interaction between



(Figure 1) Two of fourteen competing models for Ag/Si: (top) Spiegel's original CH model¹, (bottom) recent SHCT model.

the crystallographic, electronic and chemical structures producing metal induced semiconductor surface states.

The research described here attempts to answer the basic question, "How can so many good researchers from so many good labs come to such fundamentally different conclusions about the surface structure of such a simple system?". XSW and SEXAFS have been done on the surface concurrently with LEED and other surface techniques, providing information that takes account of any surface contraction effects. Additionally, we have studied the rare 3×1 to $\sqrt{3} \times \sqrt{3} R30^\circ$ phase transition in order to gain insight into the Ag surface placement.

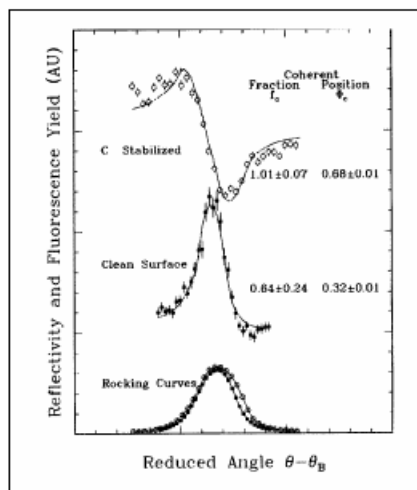
Experiments at D-line.

The XSW technique provides a measurement of atomic position relative to bulk diffraction planes and SEXAFS provides bond-length information. To study silver and silicon without the interfering effects of other atomic species, experiments must be done under ultra-high vacuum conditions. At base pressures of 8×10^{-11} torr (1×10^{-9} Pa.) and elevated temperatures of 400 to 600°C, there was a useful 18 to 24 hours experimental window before surface contamination became detectable.

A UHV beamline end-chamber was designed for use at CHESS station D-1 (see photo). Numerous pumping stages help this chamber to

reach a demonstrated 5×10^{-11} torr (0.67×10^{-9} Pa.) base pressure. (For comparison, the Wake Shield Facility recently flown on NASA's February '94 Shuttle mission achieved a vacuum of about 5×10^{-9} torr while flying outside of the orbiter.) Instrumentation on the end-chamber includes LEED, a CMA for electron analysis, a Knudsen effusion/deposition source, sample furnaces and thermometry, a movable Si(Li) fluorescence detector port, a sample load-lock mechanism, 8" diameter Be windows for entrance and exit x-ray beams, viewports, an RGA system and internal quartz IR bake-out heaters.

Experiments were conducted at CHESS' D-1 bend magnet station. Specially designed Si(111) and Si(220) four-bounce crystal sets were used to provide the wide energy range needed for Ag K (25.5 keV) SEXAFS and lower energy XSW experiments. The four bounce designed provides for detuning the two-bounce pairs to reduce the monochromator energy band-pass and allow an accurate sampling of



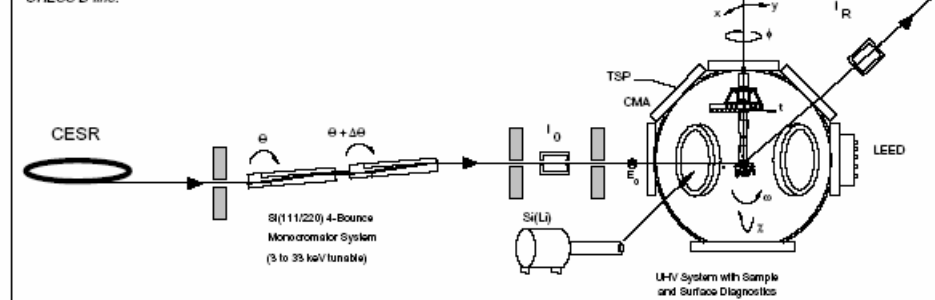
(Figure 3) XSW results for 0.2 monolayers at 400°C: (top curve) well-ordered Ag on surface with slight carbon contamination, (middle curve) carbon free surface. The different coherent fractions and atomic positions indicate different Ag structures in the two cases.

the sample's Darwin reflection curve. (These monochromator sets are available for use at CHESS' D-1 and B-2 stations.)

Results? Don't Just Expect the Unexpected — Count on it!

Two dominant factors were serendipitously found to control the surface structure. The first is carbon contamination; even slight amounts

(Figure 2) Experimental configuration at CHESS D-line.



will inhibit the formation of the 3×1 phase. Unexpectedly, we found that the structure is path dependent, that is, the method used to get to a point on the surface phase diagram can dramatically affect the resultant structure.

A few of the interesting XSW experimental results are shown in figure 3. Curves are both from surfaces with about 0.2 monolayers of Ag on Si(111) at 400°C. LEED patterns from both surfaces show a strong $\sqrt{3} \times \sqrt{3} R30^\circ$ structure; both data sets are taken from the same sample, prepared and cleaned in the same way. The difference is that one surface has trace amounts of carbon contamination which suppresses the 3×1 phase and stabilizes

the $\sqrt{3} \times \sqrt{3} R30^\circ$ Ag phase. The Fourier Transform (FT) SEXAFS spectrum, σ -polarization, also shows that Ag in the C stabilized surfaces is mono-positional while the Ag on the clean surfaces is multi-positional in the 3×1 and $\sqrt{3} \times \sqrt{3} R30^\circ$ phases. Depending on the path taken through the surface phase diagram and surface cleanliness, one can get a single nearest-neighbor bond length to dominate or, at other times, a three peaked structure to appear where there is bulk-like Ag behavior and multiple, but close, nearest neighbor distances.

Does this help explain the disparity in results of the last 27 years? Certainly! Normally reported in the literature is the final coverage and

temperature conditions of a test, but rarely the path taken to get to that endpoint. Once a method is found to reach that endpoint, the same path to that endpoint is typically taken, reducing the number of variations introduced in the procedure. Each experiment becomes self-consistent.

It may be possible that many experiments, different as they are, may be correct! We may not be closer to understanding the Ag-Si interaction but these recent results suggest areas in which greater care must be exercised in the future.

¹ K. Spiegel, *Surf.Sci.* 7 (1967) 125.

² R.J. Wilson and S. Chiang, *Phys.Rev.Lett.* 58 (1987) 369.

³ E.J. van Loenen, J.E. Demuth, R.M. Tromp and R.J. Hamers, *Phys.Rev.Lett.* 58 (1987) 373.