Surface Interactions in Heteroepitaxy : Laminar, Crystalline Silicon on CaF_2

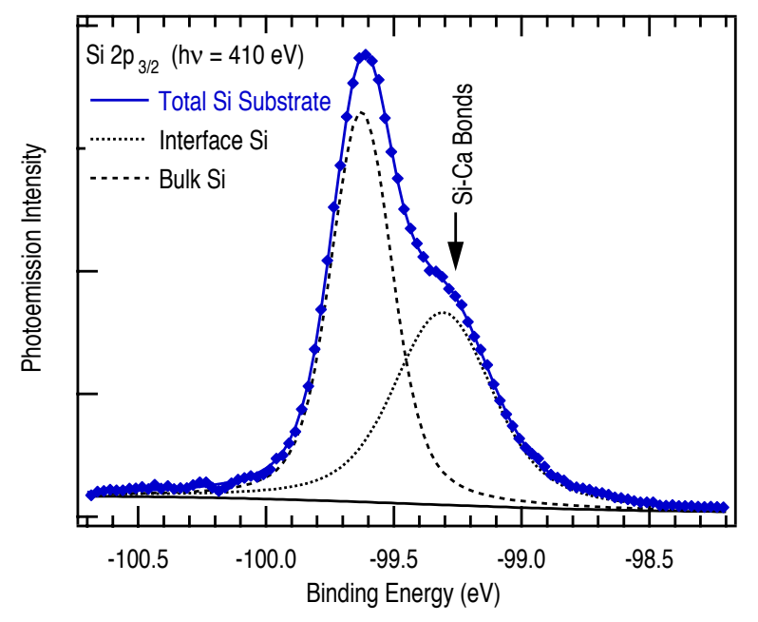
Brett Schroeder, S. Meng, A. Bostwick, E. Rotenberg *, Marjorie Olmstead
Department of Physics, University of Washington, Box 351560, Seattle WA 98195-1560
*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA 94720

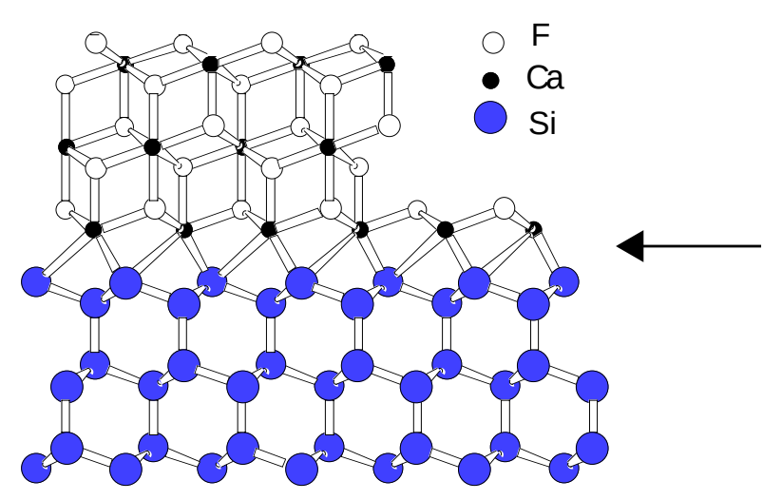
Introduction and Background

Motivation Silicon-calcium fluoride quantum wells are a strong candidate for a silicon based, visible light emitting optoelectronic device. Strong intra-conduction band transitions are predicted at optical communications wavelengths for certain silicon layer thicknesses. The development of such quantum wells also allows for the basic study of the heteroepitaxy of vastly dissimilar materials - silicon being a covalently bonded semiconductor while calcium fluoride is an ionic insulator. However, both materials have a cubic lattice and a small (0.6%) lattice mismatch at room temperature. A prerequisite of producing such quantum wells is that the growth of CaF_2 on Si and that of Si on CaF_2 be well understood. This, however, is not the case; only the growth of CaF_2 on Si is well understood.

GOAL To produce (by MBE) flat, high crystallinity Si films on CaF_2 with a well defined interface structure.

CaF_2 on Si The CaF_2/Si(111) system has been extensively studied. It is known that at growth temperatures above 550°C that the interface Si forms covalent bonds with calcium atoms. Relative to bulk CaF_2 this is non-stochiometric interface - bulk CaF_2 has a F-Ca-F stacking sequence in the [111] direction, while at the interface the stacking sequence is Si-Ca-F followed by repetitions of F-Ca-F. Thus there is a “missing” layer of fluorine atoms at the interface. X-ray photoemission of the Si2p core level shows a component 0.3 eV to lower binding energy - this is attributed to Si-Ca interface bonds.

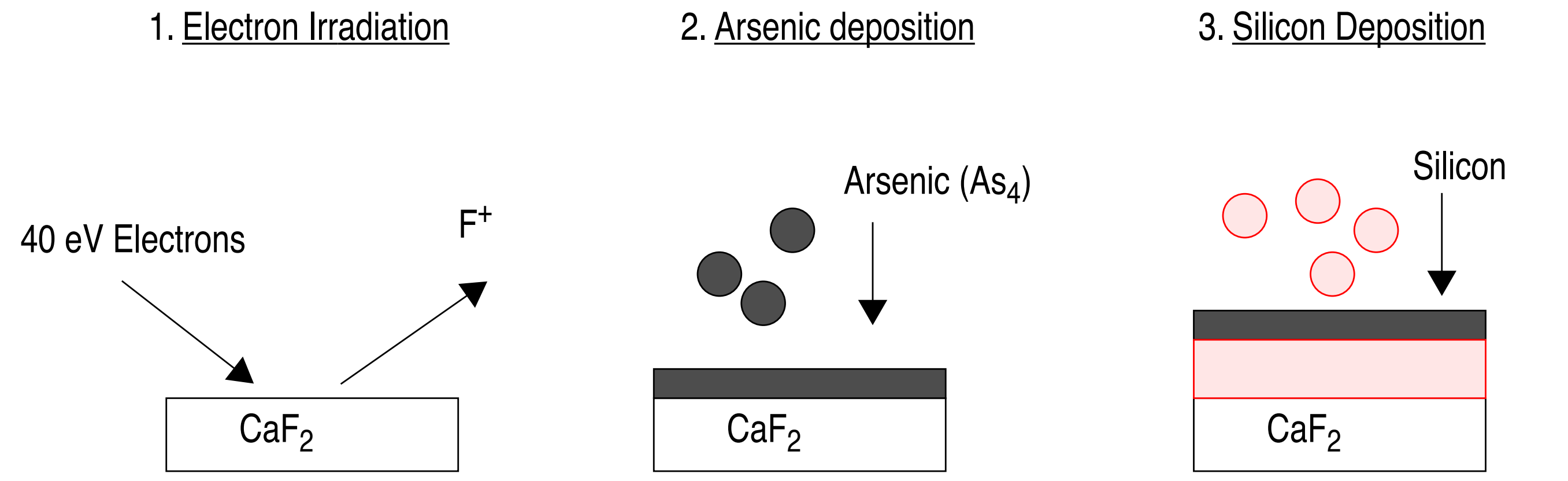




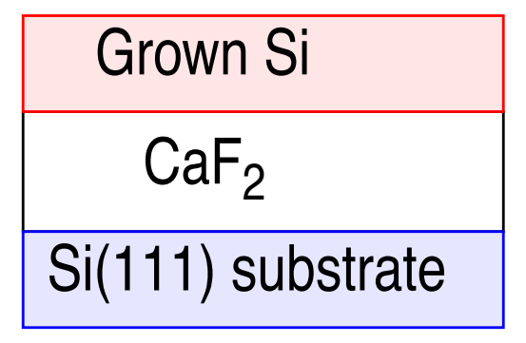
“Missing” layer of F atoms relative to bulk CaF_2

Difficulties of Si on CaF_2 The growth of Si on CaF_2 is complicated by two factors
1) Large difference in surface energies causes Si to island at intermediate (200-500°C) temperatures. Lower temperatures produce flat but amorphous films.
2) Strong Si-F chemical reaction at temperatures in excess of 550°C. This leads to an etching of fluorine from the surface followed once again by islanded Si growth. However, the islands are now capped with calcium.

Proposed Solution If we assume that the Si/CaF_2 interface will have the same structure as the known CaF_2/Si interface, then it is necessary to remove the upper layer of fluorine prior to Si deposition. This has the added advantage of eliminating the strong Si-F etching reaction. Low energy electron irradiation can be used to remove the surface fluorines. However, this defected surface is now very sensitive to impurity absorption, particularly H_2O and O_2, even under UHV conditions. The surface can be passivated with Arsenic, which only sticks if F-center defects are present. The As should also act as a surfactant during the subsequent silicon deposition, thus further limiting any islanding effects.



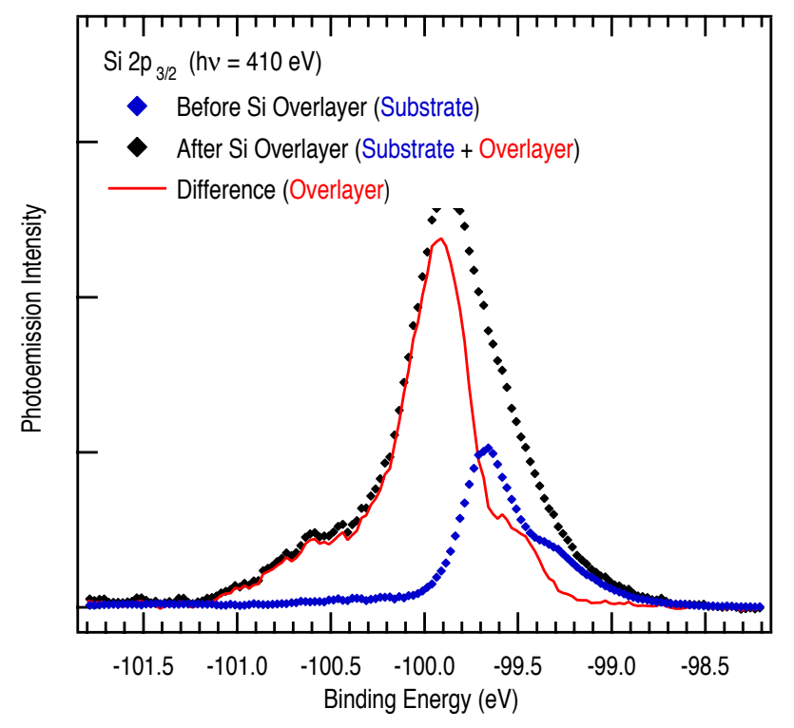
Experiment

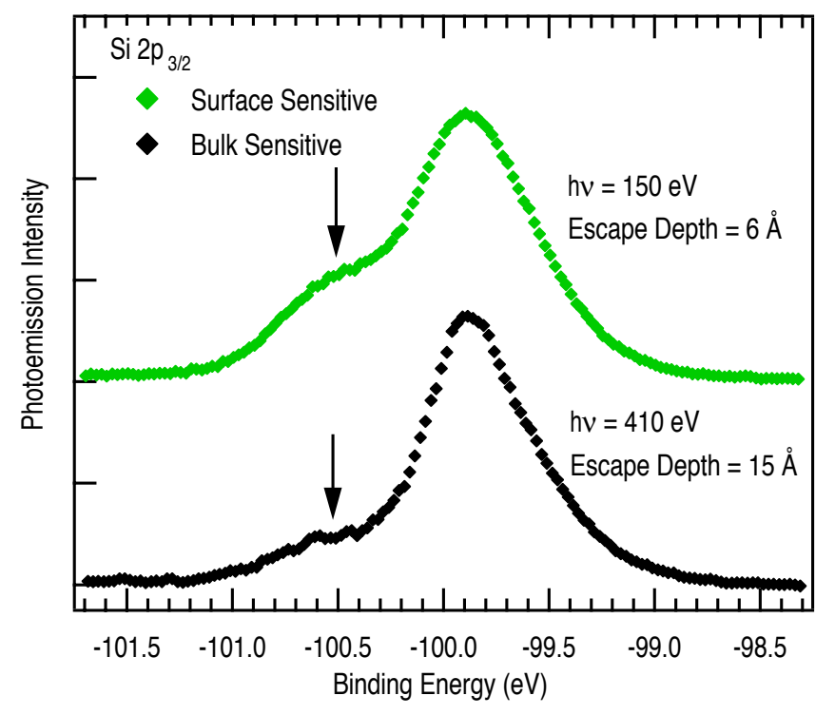


1. Five monolayers (16 Angstroms) CaF_2 grown on p-type Si(111) substrates. The experiments are performed on Si(111) substrates since these are easier to heat and cheaper than CaF_2, also, XPS charging problems are avoided. CaF_2 flux and temperature were chosen to produce a flat CaF_2 film.
2. Remove approx. 1 monolayer fluorine (40 eV electrons).
3. Deposit Si in background Arsenic flux - background As pressure = $1X10^{-8}$ Torr. This was done to resupply As to the growth surface that may have been lost due to diffusion into the CaF_2 or to a non-perfect surfactant effect. Substrate Temp = 550°C. Total Si deposition was 3-4 bilayers (9-12 Å).

Interface and Surface Chemistry

Silicon 2p XPS spectra were collected before and after growth of the silicon overlayer (spin orbit deconvolved spectra are shown here for clarity). Since the CaF_2 layer was thin, the underlying silicon substrate was still “visible” in the post silicon growth spectra. In order to determine the spectra from the overlayer only, the substrate spectrum was attenuated by the estimated thickness of the grown silicon and then subtracted from the post si growth spectrum. The resulting difference is then attributed to the Si overlayer as shown below. This overlayer spectrum exhibits several qualitative and quantitative features.

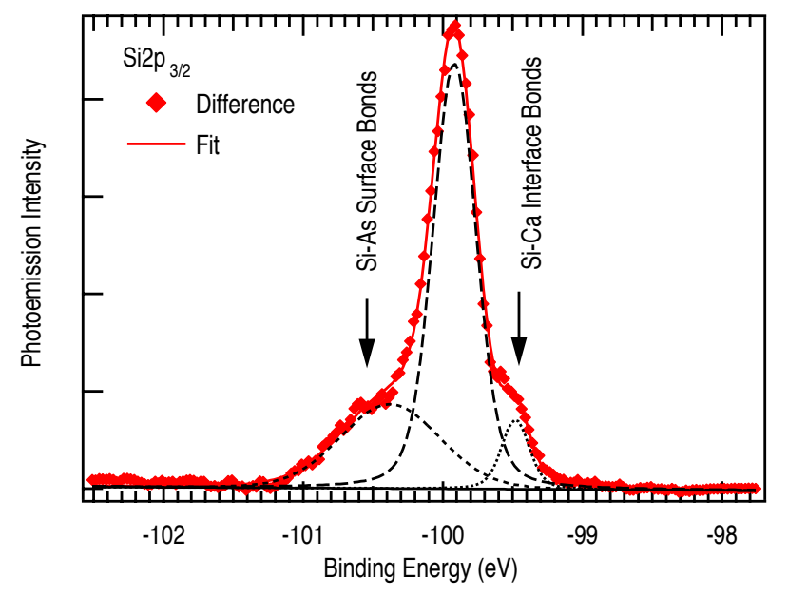




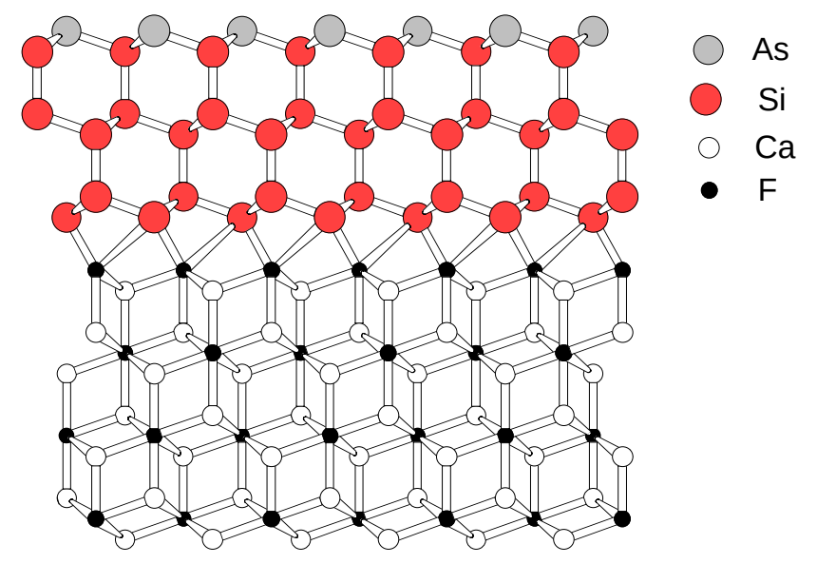
1. Low binding energy shoulder - This is similar to the shoulder observed for the CaF_2 on Si interface. This shoulder has the same separation (about 0.3-0.4 eV) from the main peak and is thus also attributed to Si - Ca bonds at the Si on CaF_2 interface

2. The overlayer exhibits an overall shift of 0.35 eV to higher binding energy relative to the substrate (measured between the peak maxima). This difference in band alignment is caused by different Fermi level positions in the overlayer and substrate. The substrate is p-type while the overlayer is expected to be heavily n-type since it was grown in a constant As background. Thus the Fermi level will be closer to the conduction band minimum in the overlayer.

3. High binding energy shoulder - This shoulder makes up a larger fraction of the spectrum at lower kinetic energies (green vs black spectrum above) and is thus associated with a surface feature. It is separated by about 0.75 eV from the main Si peak. This is the expected shift for both Si bonding the 3 arsenic atoms on the surface and Si bonding to one fluorine. Since LEED exhibited a 1X1 pattern for this surface and F does not exhibit any stable reconstructions on Si(111), this shoulder is assigned to Si - As bonds at the surface. The gaussian width of this fitted peak is wider than that of the main peak (0.8 vs 0.3 eV, all lorentzian widths forced to be equal, spin orbit parameters fixed and equal). This could be due surface disorder or components of Si bonding to 2 or 1 As atom/s (due to heavy doping) with smaller binding energy shifts.

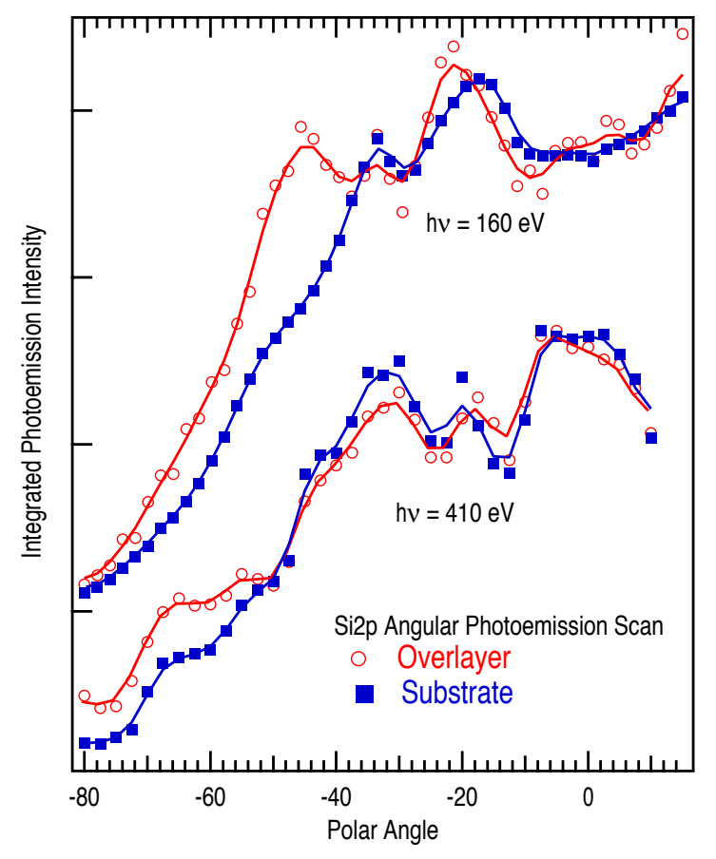


Model of Si on CaF_2 Interface and Grown Silicon

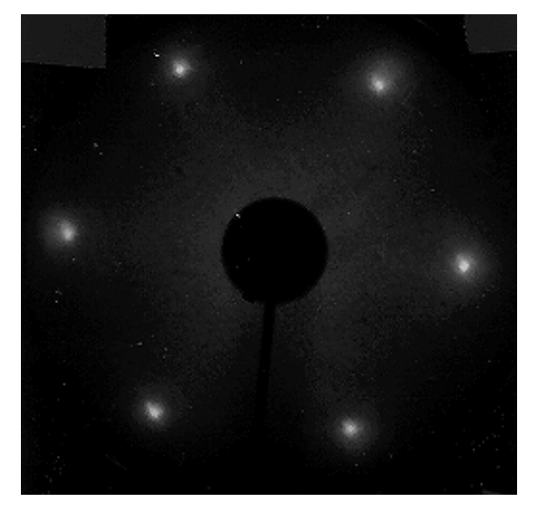


Atomic Structure

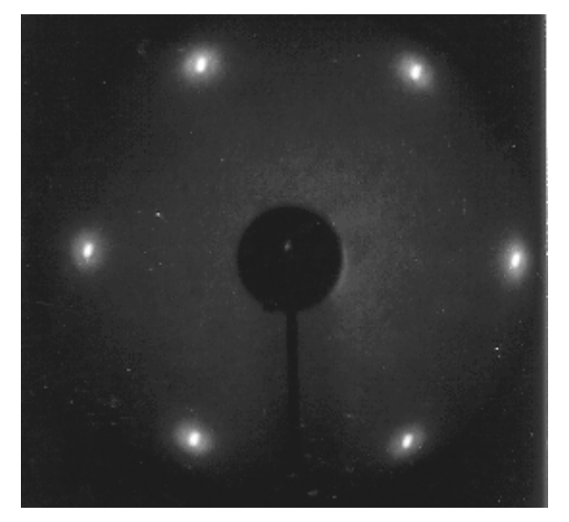
Angular dependent photoemission shows that the overlayer has the same crystallographic orientation as the substrate and is thus rotated 180° with respect to the CaF_2 (the CaF_2 is Type B on the Si(111) substrate). At both high and low kinetic energies the angular dependence of the two silicon components is similar but the substrate shows more attenuation at larger polar angles. This attenuation is more noticeable for the lower kinetic energy where the escape depth is smaller. These measurements were made by recording the intensity in two 100 meV wide portions of the spectrum that were dominated by either the substrate or overlayer.



LEED exhibited a 1X1 pattern on the grown overlayer and showed no time dependence. The lack of time dependent spots is an indication that the Si overlayer has completely covered the CaF_2 surface. When LEED is performed on a CaF_2 surface the spots change in time (intensity and sharpness decrease noticeably within 30 seconds) due to electron stimulated desorption of fluorine. The LEED image from the overlayer exhibited broader spots and a brighter background than that from an arsenic terminated silicon 7X7 surface, indicating that the coherent regions are smaller in the grown overlayer.



LEED from As terminated
7X7 surface on a commercial
wafer (48 eV)



LEED from the grown overlayer (48 eV)

Conclusion

Using a combination of electron irradiation to modify the surface stochiometry and a surfactant it is possible to grow flat crystalline silicon on calcium fluoride substrates. The grown silicon layer

1) bonds to calcium at the interface and is arsenic terminated
2) is crystalline and covers the CaF_2 substrate and
3)has a Type B orientation with respect to the CaF_2 substrate

Future Work

1) To quantify the degree of islanding during the growth of the first few monolayers
2) Attempt the growth without the background pressure of arsenic, using only1 monolayer of As as surfactant on the irradiated surface.
3) Investigate the “long” range order of the As terminated silicon layer using a combination of LEED and ultraviolet spectroscopy
4) Measure the electronic properties (band structure) of CaF_2/Si/CaF_2 quantum wells.

Funding provided by Department of Energy