

CHAPTER 5 DISCUSSION AND CONCLUSIONS

5.1 General Summary of results

The results presented in the previous chapter can be summarized as follows.

- It has been established that the starting surfaces were well-prepared with levels of contaminants on all samples studied within acceptable limits.
- RBS measurements and RUMP simulation analysis on all interfaces studied yielded consistent, reproducible results that can be used to confirm or refute structural model predictions.
- A somewhat unexpected ion beam-induced Cs desorption phenomenon was observed from the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B surfaces. A straightforward method for calculating initial saturation coverage taking desorption into consideration, was utilized.

5.2 Implications of 0.5 ML Cs coverage for the Cs/Si(100)-2×1 system

The data clearly refutes models requiring room temperature saturation coverage of 1 ML such as the Abukawa and Kono¹ model. The half monolayer coverage found is fully consistent with the Levine² model and other possible models with two or more

binding sites. Recent surface x-ray diffraction studies by Meyerheim *et al.*³ have

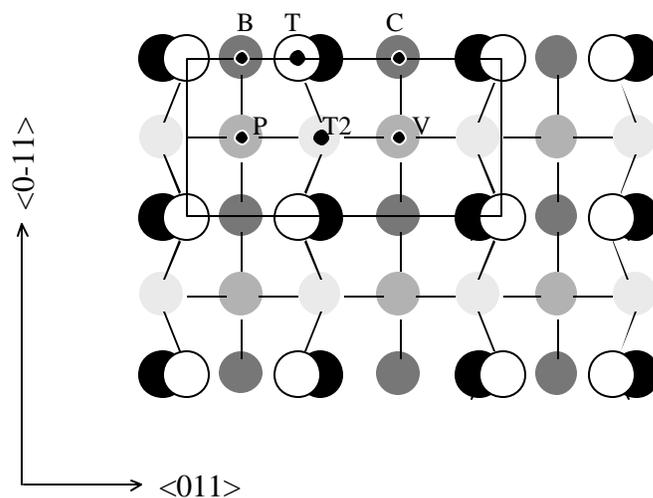


Figure 5.1 Binding sites for Cs on the Si(100)2 \times 1 reconstructed surface

suggested that the saturated cesium layer might be composed of several partially occupied sites. In particular, they suggested that Cs partially occupies five different sites: above, below, or on the dimer bridge site (B in Figure 5.1), or above or below the valley site (V in Figure 5.1). If there are several possible binding sites with none of them being significantly preferred or dominant over another, then it is possible that several different partially filled binding sites add up to yield a half monolayer coverage which would also explain two peaks in the cesium thermal desorption spectrum,⁴ and the multiple peaks in the photoelectron spectroscopy data.⁵ Even the Levine model may be consistent with

multiple binding energies by assuming that the buckling is not removed by Cs adsorption but instead give rise to asymmetric binding sites with differing binding energies. As for explaining the metallic nature of the surface several configurations of Cs atoms on the surface can be thought of that could result in the formation of conducting alkali metal chains.

5.3 Implications of 0.5 ML Cs coverage for the CsSi(111)-7×7 system

A 0.51 ML coverage, on the 7×7 surface, mean 24-25 cesium atoms are present per 49 silicon atoms in the unit cell. This means there are about 6-7 more cesium atoms than the 18 dangling bonds, so other sites are also likely to be occupied. This seems to refute the Magnusson⁶ model in which Cs should only bind with the 18 dangling bonds.

Other experimental studies using X-rays standing waves (XSW) led Eteläniemi *et al.*⁷ to propose a model for the unannealed Cs/Si(111) 7×7 surface where there was no strongly preferred binding site but a mix of all of them with a moderate preference for on top sites over rest atoms (denoted by A in Figure 5.2) and three fold coordinated sites (denoted by B in Figure 5.2) accompanied by the reordering or removal of some of the Si adatoms. The preferences for these sites are reinforced by an observed increase in the ratios of the three fold sites at the expense of the on top site after annealing.

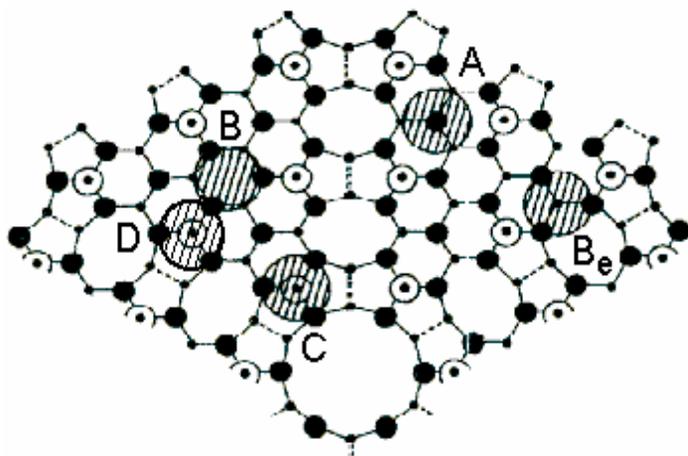


Figure 5.2 Binding sites for Cs on Si(111) 7×7 reconstructed surface.⁸

In the 7×7 surface unit cell there are 6 A type binding sites, 2 B type binding sites, 9 B_e type sites, 6 C type sites and 6 D type sites. With ~25 atoms expected to bind to the various sites if we adopt a preferential filling scheme for the B, B_e sites followed by A sites and then the others we get 11 (2B+ 9B_e) three fold symmetry sites 6 on top sites and 8 random sites This yields a ratio of 44% for three fold symmetric sites, 24% for the on top sites and 32% for the other sites which is fairly close to the ratios obtained by Eteläniemi *et al.*⁷ Even otherwise the coverage of .5 ML implies multiple partially filled binding sites which is in general agreement with the basic assumptions of Eteläniemi.

The area of the 7×7 unit cell for Si is 625.6 Å². If we assume a large covalent radius of 2.62 Å for Cs, then a close packed arrangement of 25 Cs atoms would cover an area of 594.5 Å² assuming that they were all in the same plane. If we consider square packing for the Cs atoms then the area turns out to be 686.4 Å². Thus the area of the closed packed arrangement falls slightly short of the area of the 7×7 surface unit cell,

whereas the area of the square packed arrangement exceeds it. Actually the effective area of adsorption on the 7×7 unit cell is expected to be even smaller than its area because some of the regions are not good binding sites so a fairly dense arrangement of the Cs adatoms with a partially ionic character is implied. This is consistent with the metallic nature of the surface.

5.4 Implications of 0.33 ML Cs coverage for the Cs/Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B system

Unlike the other surfaces, Cs on Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B exhibited marked desorption during RBS ion beam measurements. This implies a lower binding energy of Cs on this surface compared with the other surfaces. This is not unexpected since the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B surface is more passivated compared to the other surfaces studied; it is proposed that the Cs attaches to 0.33 ML of empty Si dangling bonds protruding from the surface layer. A relationship between the desorption cross-section, or yield, and the binding energy can, in principle, be modeled similar to work on sputtering processes taking into consideration the fact that the binding in this case is much weaker. A vastly simplified relationship between sputtering yield and binding energy of atoms can be characterized by semi empirical relationship⁹:

$$Y = \frac{0.1 E_x}{BE \cos \theta}$$

Where Y is the sputtering yield expressed in atoms per incident ion and E_x is the stopping power of the ions in the bulk expressed as eV/cm^2 , BE is the binding energy of the sputtered atoms in eV and θ is the angle of incidence of the incoming ions. The relationship can be understood in the following way: A certain fraction of the energy flux of the incoming ions which depends on the mean free path of the beam through the material contributes towards breaking the bonds and freeing an atom from the bulk. The stopping power E_x however is a macroscopic property and may not be useful for the monolayer regime.

If we assume that desorption of Cs is caused by interaction between one Cs atom and ion particle only, then we should expect a uniform scattering cross-section, which is independent of coverage, i.e., the desorption yield would simply be proportional to coverage. A simple first-order exponential decay model however may not be adequate in describing the dynamics of collision-induced desorption from a layer where nearest-neighbor interactions may play a part. In fact the data seem to suggest that the desorption cross-section appears to decrease as the atomic layer is depleted. In reality, a better understanding of the dynamics of desorption is only possible with a very detailed model supported by extensive data which is beyond the scope of the current study. However the trend in the existing data does suggest, that for high coverages the incoming ion interacts with more than one Cs atom and that the cross-section decreases with decreasing coverage because of lowered interaction with neighboring Cs atoms. This would tend to support models, which are similar to thermal shock models for sputtering at high

coverages. At sparse coverages with no interaction between the atoms a constant desorption cross section depending only on the binding energy between adatom and adsorbate, would either gradually or abruptly take over. In fact, the Cs/Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B interface could be a model system with which to understand dynamics of sputtering or desorption at an atomic scale and test existing models.

5.5 Implications of Cs coverage on Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B surface

RBS measurements of the saturation Cs coverage on the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B surface have been made and found to yield an absolute coverage of $\sim 1/3$ ML. This coverage was consistently found on several different samples involving separate RBS experiments. Unlike other techniques and probes used earlier, this is the first direct observation of the absolute Cs coverage for this surface and supports an adsorbate structure which was a critical assumption for previous studies of electronic excitation spectra¹¹

As discussed earlier in 2.4-e, indirect observations of surface structure have been made using techniques like LEED and photoemission spectroscopy techniques STM and X-ray techniques. It is well known that the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B reconstructed surface is a highly passivated surface compared to the other reconstructed surfaces of silicon. This is because of the presence of the trivalent boron atom in the subsurface layer, which is forced to interact with four neighboring Si including the surface adatom

and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -B phase is formed due to backbonding of a Si orbital to a second layer B atom reducing the energy of the surface. The persistence of the $(\sqrt{3} \times \sqrt{3})$ LEED pattern even after alkali-metal deposition indicates that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -B-induced surface structure does not change.¹⁰ ARUPS and core level spectroscopy studies of $\text{Si}(111)(\sqrt{3} \times \sqrt{3})R30^\circ$ -B reinforce the fact that the Si adatom geometry remains unaffected¹¹. If one takes this structure into account, a single empty dangling orbital is expected per $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface unit cell. Keeping the above observations and considerations in mind, it is concluded that the Cs atoms bond directly with the surface dangling bond giving rise to one Cs atom per surface unit cell with an expected charge transfer from the Cs atoms to the underlying surface. *This structural model corresponds to a coverage of 1/3 ML, and the RBS measurement is thus consistent with a structure wherein a Cs atom attaches itself to every empty dangling orbital.*

EELS, ARUPS¹¹ and work function measurements have shown that the alkali-metal covered $\text{Si}(111)(\sqrt{3} \times \sqrt{3})R30^\circ$ -B surfaces undergoes a transition from semiconducting to metallized state with an increasing coverage level. At coverages below saturation, the surfaces are semiconducting. At coverages above saturation, which is achieved by cooling the sample below room temperature with subsequent deposition, the surface ultrathin film is metallic having formed a Cs multilayer. It should be noted that the room temperature saturation coverage the properties of Na, Cs and K surfaces

differ due to their differing tendencies towards multilayer formation and their different radii which limits overlap therefore tending to electron localization for a single layer.

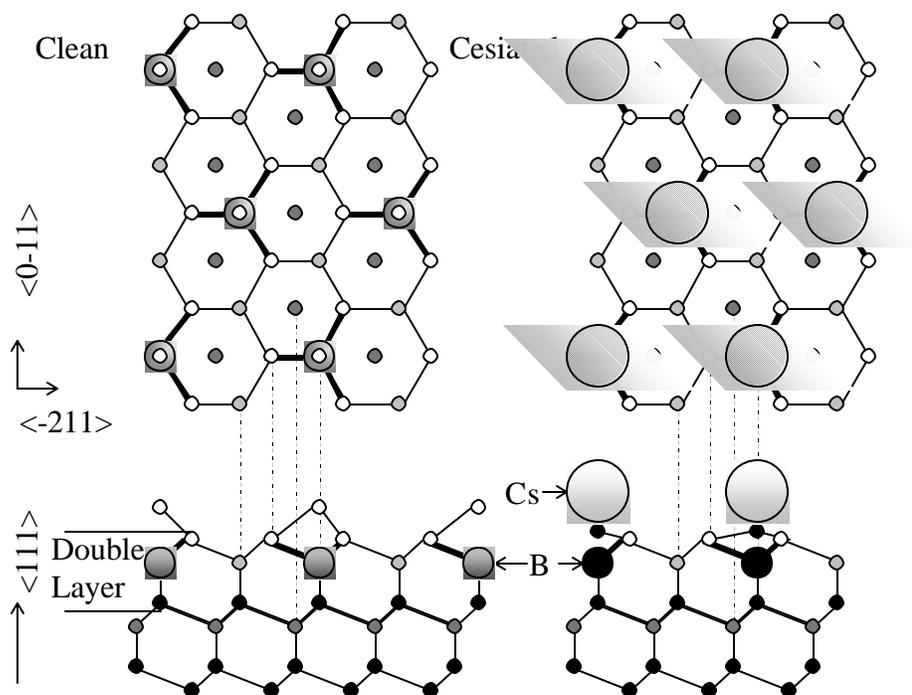


Figure 5.3 Proposed model for the Cs/Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B interface.

At saturation coverage, K is semiconducting, whereas Cs and Na are metallic, the latter due to multilayer formation. In particular, the metallic nature of Na-covered surface is evidenced by a surface plasmon loss feature observed on the Na surface during EELS studies.¹¹ A corresponding surface plasmon is not detected for the Cs-covered (or K-covered) surfaces, which means that Cs (and K) probably forms a single saturated layer.

Since a charge transfer between the alkali metal atom and the surface layer is surmised for these interfaces we can assume that the atomic radii of the alkali metals would be close to their ionic radii. The Cs metallization can be explained by the fact that the atomic radius of the Cs atom is large compared to the inter-atomic distances on the surface. On the other hand, the atomic radius of Na is small compared to the inter-atomic distances on the surface. A larger atomic radius facilitates easier flow of electrons between the surface Cs atoms leading to metallization of the surface. The RBS measurement indicates that a saturated Cs layer is not multi-layered and therefore its metallic nature is due to the large atomic radius of Cs.

This also explains why the metallization of the K-covered surface is not observed. It is because the atomic radius of K is small compared to the inter-atomic distance on the surface unlike for Cs and also because multi-layer formation does not occur at saturation coverage like it does for Na.

The origin and nature of the empty dangling surface orbitals on the $\text{Si}(111)(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-B}$ reconstructed surface suggest that any bonds formed with the orbitals will be weak. We indeed see evidence of a very weak bonding in our RBS studies. The initial maximum coverage of $1/3^{\text{rd}}$ ML decreases on subsequent exposure to the ion beam with which the RBS measurements are made. This means that the interactions between the ion beam particles and the surface Cs atoms are energetic enough to break the bond. This degradation of coverage during exposure to the ion beam is not observed in the case of the other reconstructed surfaces of the $\text{Si}(111)$ and $\text{Si}(100)$

crystal faces, which means that the bonds between the Cs atom and the surface are much stronger for those surfaces.

5.6 Further Work

While the above experiments shed new light on alkali-metal – semiconductor interfaces, additional insights can be gained by studying other alkali-metal – semiconductor interfaces (different alkali-metals and different surface reconstructions) in more detail. Besides direct coverage measurements with RBS, Medium energy ion scattering (MEIS) experiments with channeling and blocking could in principle provide key information on structure of the surface layer and underlying bulk layers provided order exists. The current RBS coverage measurements carried out in the study narrows down the possible surfaces models but still leaves possibilities open as to the actual surface structure.

An interesting desorption phenomenon was observed for the Cs/Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B surface which could be further investigated. The desorption cross-section for the Cs atoms will give an idea as to the binding energy, possibly in conjunction with Thermal Desorption and angle-dependent measurements.

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