

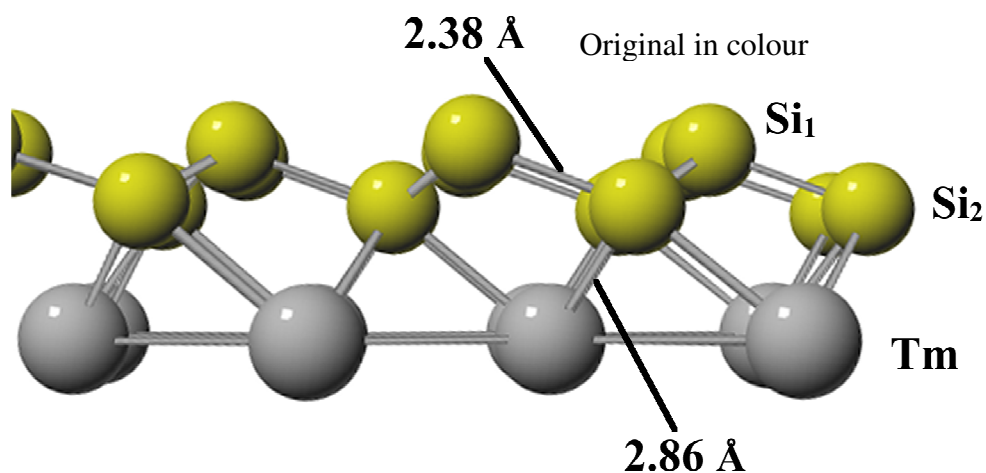
## Chapter 8

### Conclusion

The Tm/Si(111) surface has been studied using the technique of medium energy ion scattering. The structure of the Tm silicide has been shown to be similar to that of other known rare earth silicides and a comparison of the structural parameters with those of the other RE silicides has revealed a trend across the series. Some problems with the common method of performing R-factor analysis of the MEIS data have been identified and remedies investigated. MEIS has also been used to study the initial growth of Fe on the Si(111) surface, in the monolayer regime. A structural model for the silicide formed has been proposed. The surface of the rare earth silicides has been further investigated. Scanning tunnelling microscopy has been used to study the electronic structure and their possible use as growth templates has begun to be studied using MEIS.

#### 8.1 MEIS Study of Thulium Silicide

A quantitative MEIS study of Tm growth on the Si(111)  $7 \times 7$  surface in the monolayer regime has been performed. Deposition of 1 ML of Tm followed by anneal at  $\sim 500$  °C formed a silicide which exhibited a  $1 \times 1$  LEED pattern. The MEIS data confirmed that the structure of this silicide is very similar to the known structure of other RE silicides. These silicides consist of a single layer of RE beneath a bulk-like Si bilayer which is rotated by  $180^\circ$  with respect to the bulk. A structural model of the Tm silicide formed was constructed based on this known basic structure. Comparisons to the experimental data of Monte Carlo computer simulations of ion scattering from the Tm confirmed such a structure. Further, comparison to multiple models allowed a quantitative determination of structural parameters, although some problems in the fitting procedure (discussed below) were identified. The bond length between the Si atoms within the



*Figure 8.1: Side view of the Tm 2D silicide structure indicating the bond lengths. Bulk Si has been omitted for clarity. The silicide consists of a single RE layer beneath a bulk-like Si bilayer. The bilayer is rotated by 180 ° with respect to the bulk.*

terminating bilayer was found to be  $2.38 \pm 0.02 \text{ \AA}$  (a 1.3 % expansion compared to the bulk Si bond), with a bilayer Si–Tm bond length of  $2.86 \pm 0.02 \text{ \AA}$  (Figure 8.1).

## 8.2 Structural Trends in 2D Silicides

The structural result for two dimensional Tm silicide has been compared to that for other 2D silicides. Initially it appeared that the structure of Tm silicide did not fit the trend evident from other RE silicides. However, further consideration revealed that the problems inherent with fitting simulations to the Tm experimental data were also present, unspotted, in the case of the other RE silicides. This may have affected the results published in the literature. These problems have been further investigated, as summarised in Section 8.3.

Such careful consideration of the structural parameters of the series of rare earth 2D silicides has led to the identification of a trend across the series. Though inherent problems have been identified in the fitting of the data to simulated models, the weight of evidence still makes a convincing argument for the trend,

even if the absolute values of the bond lengths remain uncertain. Due to the unusual nature of the 2D silicide scattering data—in which the Si–RE bond is represented by a single blocking dip—the trend can be visually discerned by comparison of the data from each of the silicides. Indeed, visually fitting simulation and experiment also reveals the trend.

As the RE mass increases the Si–RE bond length contracts slightly, decreasing by around 2 % across the series. This trend reflects that seen in the RE–Si bond lengths of bulk rare earth silicides. The Si–Si bond within the terminated bilayer remains approximately constant.

### **8.3 R-factor Analysis of MEIS Data**

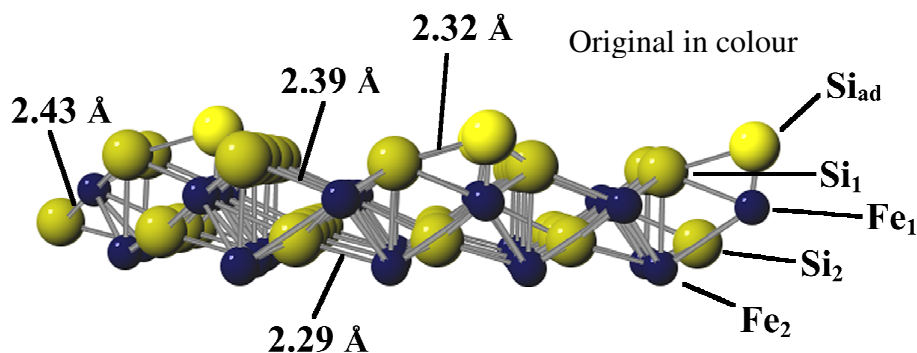
As briefly discussed above, problems were identified in the common method of comparing experimental MEIS data to computer simulations using a  $\chi^2$  R-factor. It was found that in the case of the 2D silicides the simplicity of the scattering curves allowed a reasonable comparison of experiment and simulation to be performed by eye. This revealed that the fitting of the experimental blocking curves to the simulations by the  $\chi^2$  R-factor was not the best possible. Further investigation showed that this particular form of R-factor placed too much emphasis on the fitting of blocking features at lower scattering angles. More specifically the R-factor over emphasised the fitting of the blocking dip depth whilst neglecting the fitting of the angular position of other features. In the specific case of the 2D RE silicides this had the effect of producing a poor fit to the scattering angle of the higher angle blocking dip, which corresponds to the Si<sub>2</sub> atomic position. It is this unusually straightforward correspondance between an individual blocking dip and an atomic position which makes the 2D silicides an ideal case for identifying and investigating such problems. It is noted that there is no guarantee that such problems do not exist in the comparison of more complex scattering curves, however, and that this represents an important issue for the MEIS community in general.

Several other R-factors were investigated to try and identify a more reliable

comparison technique. No completely satisfactory method was found, though a combination of methods could at least give some confidence in the overall results. A form of R-factor based on the Pendry R-factor of LEED analysis shows the greatest promise for a more permanent solution.

#### 8.4 Iron Growth on Si(111)

While the Fe–Si interface has been well studied there is still little known of the crystallographic structure in the monolayer regime. The initial growth of Fe on the Si(111) surface was studied using MEIS. At a coverage of  $\sim 1.7$  ML two phases—a  $1 \times 1$  phase and a  $2 \times 2$  phase—were observed by LEED, depending on anneal temperature. The  $1 \times 1$  phase was observed after annealing at around  $300^\circ\text{C}$  and the  $2 \times 2$  phase at higher anneal temperatures ( $\sim 500^\circ\text{C}$ ). MEIS data was acquired from both phases and showed that the two are structurally extremely similar. Ions scattered from Fe atoms were seen to be blocked at characteristic angles in a number of geometries. Based initially on considerations of the location of these dips a structural model was derived. Comparison of the data with computer simulations has led to the confirmation of this structural model. The model is based on a CsCl-type structure with the bonding direction of the silicide reversed with respect to the bulk bonds. The  $2 \times 2$  phase is formed by



*Figure 8.2: Side view of the Fe silicide, showing the  $2 \times 2$  Si adatom layer and indicating bond lengths. Bulk Si has been omitted for clarity. The silicide is a CsCl-type structure with, in the case of the  $2 \times 2$  phase, an additional layer of Si adatoms in a  $2 \times 2$  arrangement.*

the addition of an ordered Si adatom layer atop the  $1 \times 1$  phase. Multiple computer simulations allowed this model to be refined. The surface model and bond lengths found are shown in Figure 8.2.

## 8.5 Studies of the Silicide Surface

### 8.5.1 *Iron Growth on 2D Silicides*

As mentioned above two dimensional rare earth silicides have been well studied over the last few years and the structure is now well established. The novel surface offered by these materials has potential as an interesting growth template, both from a fundamental science point of view and with respect to possible technological applications, such as in the field of spintronics. An initial MEIS study of the growth of Fe on 2D Ho silicide was made. On deposition of around 1.7 ML Fe immediate disruption of the interface was seen. Progressive annealing failed to restore an ordered surface, merely resulting in the migration of the Fe, and eventually Ho, into the bulk substrate. However, the presence of slight oxygen contamination may have played a roll in the experiment, as O is known to disrupt the RE 2D silicide surface.

### 8.5.2 *STS of 2D Silicide*

The electronic structure of the 2D silicides has also begun to be investigated. The 2D Ho silicide surface has been studied by atomically resolved STS. It has been found that unusually no difference between STS data from inequivalent sites could be detected, indicating a delocalised surface state. The STM image obtained would thus seem to reflect the true surface topography rather than any electronic effects. The STS data was found to be in broad qualitative agreement with theoretical calculations and experimental measurements of the 2D silicide band structure.

## 8.6 Future Work

Two dimensional silicides have been structurally well established. Their use as a basis for further growth however, has only just begun. Whilst the initial investigation reported in this work was disappointing in terms of the lack of ordered structure formed, it may have been affected by unintentional oxygen contamination. The further study of Fe and other metal growth (where the growth of the metal on clean Si is better understood) on these novel silicides is certainly of interest. The possibility of further Si growth, perhaps burying the single rare earth layer, also presents itself. It is hoped that the subtle differences between the 2D silicides identified by the trend in structural parameters may be of some aid in future growth investigations.

In both metal and semiconductor growth on these RE silicide templates MEIS could prove an invaluable technique. The ability to separate the signal from each element due to the mass difference allows the rare earth signal to be used as a “searchlight” to determine the structure of the layers above it. However, for such a method to reach its full potential further investigation is needed into the problems associated with the standard R-factor comparison of simulated and experimental data. Studying the performance of various R-factors applied to the RE silicides and other systems should give a fuller understanding of the problem and its extent. Certainly it seems that a more robust approach is required. Whilst other R-factors may give greater confidence in a result a more quantitative method of error estimation is required. Perhaps there is no “one size fits all” solution in terms of reliability factor, but if this is the case a larger toolbox of comparison techniques needs to be developed, with the vigilance of the experimenter being of great importance. It is the author’s belief that it is vital to resolve these problems in order to have the fullest confidence in such simulation–experiment comparisons, especially when the blocking features are more complicated than those involved in the 2D silicide comparison.

An understanding of the formation of Fe silicide at low coverages is far from complete. The Fe silicide structure found in this work could benefit from further

MEIS study utilising carefully chosen scattering geometries. These might better reveal the Si adatoms in the  $2 \times 2$  phase as well as further differences between the  $2 \times 2$  and  $1 \times 1$  phases. As the main distinction is in the termination of the surface an STM study is suggested. This could reveal if the  $1 \times 1$  phase already has an adatom overlayer which is then ordered during the anneal to form the  $2 \times 2$  phase. It seems likely that the two phases could be found to coexist under some circumstances.