Contents

Acknowledgements iv

Abstract v

1 Introduction 1

2 Apparatus 7
   2.1 UHV chamber system ........................... 7
   2.2 Electron gun system ........................... 14
   2.3 Imaging system .............................. 18
   2.4 Sample translation and manipulation ............... 19
   2.5 Gas-handling system ........................... 22
   2.6 Femtosecond laser system ........................ 26

3 Methodology 30
   3.1 Electron crystallography ......................... 30
   3.2 Pump-probe experiment .......................... 39
      3.2.1 Characterization of the electron pulses .......... 41
      3.2.2 Alignment of the laser and electron beams .......... 44
      3.2.3 Measuring the laser fluence on the sample ........... 45
      3.2.4 Determining time resolution and time zero .......... 46
   3.3 Analysis of the diffraction patterns ................ 48

4 Studies of Single-Crystal Surfaces with Small Adsorbates 51
   4.1 Silicon(111) surface ............................ 52
5 Fatty Acid and Phospholipid Crystalline Adsorbates:

Steady State Studies

5.1 Langmuir-Blodgett films of fatty acids and phospholipids
5.2 Preparation of layers by LB deposition
5.3 Fatty acid bilayers structure
5.4 Fatty acid bilayers temperature-dependent structural change
5.5 Fatty acid multilayers structure
5.6 Phospholipid monolayer and bilayer structure

6 Fatty Acid and Phospholipid Crystalline Adsorbates:

Ultrafast T-jump Dynamics

6.1 Fatty acids structural dynamics
   6.1.1 Atomic motions in the chain
   6.1.2 Transient structural ordering
   6.1.3 Dynamics at different static temperature
6.2 Phospholipid structural dynamics
6.3 Structural dynamics picture

7 Conclusion

Bibliography
List of Figures

2.1 The chamber system with frame support. ................ 8
2.2 Schematic diagram of the experimental setup. ............... 10
2.3 Schematic side view of the sample preparation chamber and the load-lock chamber. ........................................... 13
2.4 Schematic view of the goniometer. ............................... 15
2.5 A cut through the electron gun chamber and the scattering chamber. . 16
2.6 A cut through the CCD imaging system. ............................ 18
2.7 Schematic side view of the load lock chamber and the scattering chamber. 21
2.8 Schematic view of the gas-handling system. .................... 23
2.9 The optics layout. ..................................................... 28

3.1 Schematic diagrams of Ewald sphere construction. ............. 35
3.2 Schematic diagram of RHEED experiment. .......................... 37
3.3 Schematic view of the experiment. ................................. 40
3.4 Electric diagram for the streaking experiment. ..................... 42
3.5 Result of the streaking experiment. ................................. 43
3.6 Schematic diagram of the alignment. ................................. 44
3.7 Schematic diagram of the measurement of excitation laser beam spatial profile. .................................................... 47

4.1 Structure of the Si:H(111) crystal. ................................. 52
4.2 Diffraction patterns of Si(111) surfaces. ............................ 53
4.3 The temporal change of the Bragg spot (-4,7). ..................... 55
4.4 UEC of phase transition of the amorphous to liquid state. ....... 57
ix

4.5 Structure of the GaAs:Cl(111) crystal. ........................................... 58
4.6 GaAs:Cl(111) surface lattice structure. ........................................ 59
4.7 Static diffraction images of the GaAs:H(111) surface. ................. 60
4.8 Time dependence of the Bragg reflection center position. ............... 62
4.9 Fluence dependence of the Bragg reflection center position change. ... 63
4.10 Comparison of the integrated intensity, center position and width change
     of the Bragg spot. .......................................................... 65

5.1 Structure of crystalline adsorbates of fatty acids and phospholipids. ... 73
5.2 Structure of the orthorhombic C2H4 subunit cell. ............................. 74
5.3 Directions of dipping, observation and subunit cell orientation. .......... 76
5.4 Static diffraction patterns of fatty acid bilayers. ............................ 78
5.5 Static diffraction rocking curve of fatty acid bilayers. ...................... 79
5.6 Calculated diffraction patterns. ................................................. 81
5.7 Static temperature dependent diffraction patterns. ......................... 85
5.8 Static temperature dependence of diffraction intensity and subunit cell
dimensions. .............................................................................. 86
5.9 Schematic view of the static thermal behavior. ................................. 88
5.10 Multilayer diffraction patterns. ..................................................... 90
5.11 Inclined diffraction patterns for 8-layer samples. ............................ 91
5.12 Static diffraction patterns of DMPA samples. .................................. 93

6.1 Diffraction difference frames of the (002) Bragg spot. ...................... 96
6.2 Full analysis of the (002) Bragg spot. ........................................... 97
6.3 Time dependence of the peak shift and the corresponding molecular
axial length change for bilayers. .................................................. 99
6.4 Dynamics of fatty acid bilayer compared to that of the substrate Si(111)
surface. ...................................................................................... 100
6.5 Time dependence of the molecular axial length change for 2-, 4- and
8-layer sample. ........................................................................... 102
6.6 Dynamics of the inclined 8-layer sample. ........................................ 104
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>Relative intensity change $I/I_0$ as a function of time for 2-, 4- and 8-layer samples.</td>
<td>105</td>
</tr>
<tr>
<td>6.8</td>
<td>Schematic view of the transient structural ordering.</td>
<td>107</td>
</tr>
<tr>
<td>6.9</td>
<td>Dependence of the transient dynamics on initial substrate static temperature.</td>
<td>108</td>
</tr>
<tr>
<td>6.10</td>
<td>Static diffraction and diffraction difference patterns of DMPA monolayer and bilayer.</td>
<td>110</td>
</tr>
<tr>
<td>6.11</td>
<td>The axial change $\Delta c_0$ and the normalized integrated intensity of the $(hk2)$ diffraction line as a function of time.</td>
<td>111</td>
</tr>
</tbody>
</table>
List of Tables

5.1 Lattice parameters for fatty acid bilayers. ................  82
5.2 Lattice parameters for fatty acid multilayers. ..............  89