CHAPTER 1
DIFFERENT PHASES OF WATER AND NUCLEATION OF THE ICE-PHASE

1.1 GENERAL INTRODUCTION

The Earth is unique in many ways. None of the other planets of the solar system has its vast oceans and none has an atmosphere similar in composition to that of the Earth.

Water existed on Earth long before life began and it is fundamental to most life processes. More than two thirds of the Earth is covered with water and nearly one tenth of its surface is covered with ice [1].

Water is one of the basic commodities on which our civilization depends and it is no accident that the highly developed regions of the world are those which are endowed with good supplies of water. Practically the whole of our usable water comes in the form of precipitation from the atmosphere [2].

1.2 UNUSUAL PROPERTIES OF WATER

Water is a much more complicated substance than its simple formula, H$_2$O, might indicate. Composed of two hydrogen atoms combined with one atom of oxygen (Figure 1.1), water has some very unusual properties in comparison with other commonly occurring materials.

First, water is the only substance on earth that appears in all three forms—gas, liquid and solid—at temperatures commonly found on the planet. In each of these states water
Figure 1.1 Water molecule and the relationship among molecules in the ice, vapor, and liquid states.
still consists of two hydrogen and one oxygen atom; the only difference is the organization of the molecules. In the ice phase Figure 1.1(b), water molecules are arranged completely in groups of six molecules. Because of low temperatures, the water molecules have less energy and are not free to move around. As the temperature increases, the molecules become more energetic and the bonds of the ice phase are broken. In the liquid state, water molecules are still close together, but they are free to slide around, and thus liquid water flows readily. In the gas or vapour phase, the water molecules are highly energetic and fly about in a totally disorganized manner Figure 1.1(d).

Secondly, unlike most substances, water expands just before it freezes and during freezing process. As a result of this expansion, ice floats on water rather than sinks, a fortunate property for underwater life.

A third, unusual property of water is its heat capacity, which is higher than all natural substances except ammonia. A substance with a high heat capacity requires more heat energy to increase its temperature by a given amount than does a substance with low heat capacity. Thus, raising the temperature of one gram of water by 1°C requires 1 calorie of heat input. In contrast, the same calorie of heat would raise the temperature a gram of air by more than 4°C. The high heat capacity of water is one reason that oceans and large lakes are slow to warm in spring and cool in autumn.

A fourth, remarkable property of water is the heat required to melt ice (latent heat of fusion) or evaporate water (latent heat of vaporization). To melt 1 gram of ice requires about 80 calories of heat; and to evaporate 1 gram of water requires an amazing 597 calories of heat at typical surface pressures. These values are much higher than the latent heats of most substances. Conversely, when water condenses
(freezes), it releases 597 (80) calories per gram. When the condensation or freezing occurs in the atmosphere, this heat is transferred to the air and represents an important energy source for such natural phenomenon as thunderstorms, tornadoes and hurricanes all of which depend on the release of latent heat. Finally, the evaporation of water at low latitudes and the subsequent poleward transport and recondensation at high latitudes represents a significant transfer of energy from low to high latitude [3].

1.3 STRUCTURE OF WATER SUBSTANCE

1.3.1 Structure of an Isolated water Molecule

The geometry of the water molecule can be deduced accurately from studies of the infrared spectrum of water vapour. On the basis of such measurements, Mecke (4) concluded that the three atoms are situated at the vertices of a triangle, the geometry of which is given in Figure 1.2. Experiments show that the equilibrium O-H bond length is 0.95718Å and that the equilibrium H-O-H bond angle is 104.523° [5,6].

The structure of the water molecule is importantly affected by the electron configuration around the oxygen atom. In its ground state, an oxygen atom has two electrons in the spherical 1s orbital, where they are bound tightly to the atomic nucleus, and two electrons, less tightly bound, in the 2s orbital. In addition, two electrons can be considered to occupy the 2pₓ orbital, one electron the 2pᵧ orbital and one electron the 2pₜ orbital. This electron configuration is illustrated in Figure 1.3. Since the 2pₓ and 2pᵧ orbitals may contain two electrons each, these orbitals are incomplete. The electrons in these orbitals are therefore free to couple with the
Figure 1.2 Two-dimensional geometry of a single water molecule.

Figure 1.3 Orbitals of oxygen atoms on water molecule
electrons in the 1s orbital of the two hydrogen atoms, allowing them to form two O-H bonds.

1.3.2 Structure of the Water Vapour:

Experiments indicate that water molecules in water vapour tend to interact and form clusters, in contrast to ideal gas behaviour. Dimers as well as higher order polymers are considered to be present in water vapour, though in small concentration only. Recent experiments involving molecular beam techniques [7, 8] suggest that in highly super saturated water vapour, clusters up to 180 water molecules may be present. Clusters of 21 water molecules seemed to exhibit particularly large stability. However, no conclusive evidence of the actual geometric arrangement, if any, of water molecules in such clusters in vapour is available at present. Studies on the possible and more likely cluster types have been reviewed by Rao and Kell [9, 10].

1.3.3 Structure of Ice

At atmospheric pressures and temperatures between about -100°C and 0°C water substance crystallizes from its gaseous or its liquid state to form a six-fold-symmetry or hexagonal solid called ice-Ih. At different temperatures and pressures ice assumes other crystalline modifications which are discussed, for example in Fletcher and Hobbs [5, 6].

X-ray diffraction studies demonstrate that in ice each oxygen atom is surrounded by four nearest neighbour oxygen atoms at a distance of about 2.76 \times 10^{-8} cm. These four atoms form an almost regular tetrahedron. In turn, these oxygen tetrahedrons are joined together to form a hexagonal lattice shown in Figure 1.4. The hexagonal space group is denoted by D_6^h or P6_3/mmc, and is characterized by
Figure 1.4 The arrangement of the oxygen atoms in ice Ih.
(The rods joining the oxygen atoms represent bonds. The hydrogen atoms are not shown.)
(a) View perpendicular to the c-axis
(b) View along the c-axis
1 sixfold axis of rotation perpendicular to 1 mirror plane, (3+3) twofold axes of rotation perpendicular to (3+3) mirror planes, and a center of symmetry.

Near 0° C, any given oxygen atom in ice also has 12 second nearest neighbours at a distance of about 4.52 Å, 1 third nearest neighbour at 4.59 Å, 6 fourth nearest neighbours at 5.26 Å, 3 fifth nearest neighbours at 5.31 Å, 6 sixth nearest neighbours at 6.36 Å, 6 seventh nearest neighbours at 6.46 Å, 9 eighth nearest neighbours at 6.69 Å, 2 ninth nearest neighbours at 7.36 Å, and 18 tenth nearest neighbours at 7.81 Å. (Kamb, B., 1975, personal communication).

Each water molecule is hydrogen bonded to its nearest four neighbours. This is brought about through the formation of two hydrogen (O—H—O) bonds by each water molecule, each bond being directed towards a lone electron pair of a neighbouring water molecule. This manner of bonding leads to an open lattice structure as illustrated in the Figure 1.4. Perpendicular to the c-axis, the ice lattice consists of open-puckered hexagonal rings (with oxygen atoms alternately raised and lowered). Along the c-axis are vacant shafts. Comparison shows that the arrangement of oxygen atoms in ice is isomorphous with the Wurtzite structure of ZnS and the tridymite structure of SiO₂.
1.4 PHASE CHANGES OF WATER

Phase changes of water play the primary role in microphysics of clouds. The possible phase changes are:

Vapour $\leftrightarrow$ solid (deposition, sublimation)

liquid $\leftrightarrow$ solid (freezing, melting)

Vapour $\leftrightarrow$ liquid (condensation, evaporation)

Hence ice may be formed either by deposition from vapour phase or by freezing of liquid water. In both cases the initiation of ice phase occurs by the nucleation of a small ice embryo [6].

1.4.1 Solid Phases of the water substance

Water forms more solid phases than any other known substance. If liquid water is frozen under normal atmospheric conditions or water vapour deposited at temperature below 0°C and above -80°C, the water molecules are arranged in orderly repetitive positions to form a crystalline solid with hexagonal symmetry which is referred to as hexagonal ice, ice I$_h$, or simply ice. The deposition of water vapour on to a base at a temperature between about -80 and -130°C also produces a crystalline solid, but in this case the structure is cubic and is known as cubic ice or ice Ic. In addition, at least eight high pressure crystalline forms of the water substance (ice II to IX) have been identified which we are referred as the high pressure polymorphs of ice. If water vapour is deposited on to a base at a temperature below about -140°C, the deposit appears to be either noncrystalline or to consist of very small crystals and is often referred to as vitreous or amorphous ice. There is also a large number of
structures, known as the clathrate hydrates, which are solid phases of water with large holes in them which are filled with inert molecules such as xenon argon and ethylene oxide.

1.4.2 Phase diagram for bulk water substance

The temperature variation of the saturation vapour pressure is shown in Figure 1.5. From the figure we can note that the saturation vapour pressure over plane water surface is greater than saturation vapour pressure over plane ice surface for temperature less than 0°C. The interesting point to emphasize is that air saturated with respect to ice is always subsaturated with respect to water, with the consequence that super cooled water drops and ice crystals cannot coexist in equilibrium. It is also worth emphasizing that at sufficiently low temperatures, air may be ice-supersaturated but water-subsaturated. Thus the equilibrium behaviour of bulk water has been displayed in the form of a p-T phase diagram (Figure 1.5). Complete information on the equilibrium behaviour between water vapour, water and ice in bulk may be obtained from the Figure 1.6 displayed in the form of a p-V-T phase diagram. At the top of the phase boundary curve is the critical point, where the distinction between liquid and gas vanishes. At this extraordinary point the surface tension or surface energy of the interface separating the phases becomes zero. Atmospheric water always lies far below the critical point, which occurs at $p_c = 221$ bars and $T_c = 374^\circ$C. The concept of the critical point illuminates the distinction between water vapour and other permanent, atmospheric gases.
Figure 1.5 p-T phase diagram for bulk water substance.
Figure 1.6 Three dimensional phase diagram for bulk water substance (dashed lines represent isotherms)
1.5 NUCLEATION

In cloud physics we are concerned with three principal phase changes - the condensation of water - vapour to form droplets, the freezing of water droplets to form ice-crystals and the direct formation of ice-crystals from the vapour by sublimation. These three phase-changes have an important property which is characteristic of phase-changes in any material, namely that they do not begin in a continuous manner, but require 'nucleation' [12]. Nucleation is the initial, important phenomenon in phase transformations and in solid state variations. It is the process of generating within a metastable mother phase, the initial fragments of a new and more stable phase capable of developing spontaneously into gross fragments of the stable phase.

Cloud condensation, polymer crystallization, bubble formation and bone growth are a few isolated examples of nucleation phenomena, in which each represents the birth of one phase from the other. Like ordinary chemical kinetics, it involves an activation process leading to the formation of unstable intermediate states known as 'embryos' [13-16]. When the embryo reaches a critical size, it is called 'nucleus'. A nucleus differs from an equal number of normal molecules in possessing an excess of surface energy sufficient to produce the aggregate as a new phase. This energy can be evaluated with the help of Gibbs' general formula [17]. Nucleation may occur either spontaneously or may be induced artificially. The former is quite often referred to as 'homogeneous' nucleation and latter as 'heterogeneous' nucleation.
1.6 HOMOGENEOUS NUCLEATION

Nucleation process can be divided into two main classes. Suppose we have a quantity of pure water-vapour and cause it to become super saturated either by closing it, or by compressing it isothermally. To attain the state of lowest energy the vapour should now condense, but this condensation process must commence with the formation of small droplets, and these are unstable under the buffetings of thermal agitation. The vapour thus remains in its metastable gaseous state and no condensation takes place. As the supersaturation is increased small droplets become more stable, and the likelihood of their survival increases, until at a certain critical supersaturation the survival rate becomes appreciable and condensation to a fog takes place. Such a nucleation process occurring within the bulk of a pure substance is referred to as ‘homogeneous nucleation’, and is characterized by the rather high degree of super saturation required for it [12].

1.6 HETEROGENEOUS ICE-NUCLEATION

If the super saturated vapour is confined in some sort of container, then the walls of the container may provide sites where condensation occurs more easily than in the bulk of the vapour. Similarly, if the vapour is contaminated with small particles of airborne dust these may serve as nuclei for the condensation of water droplets. In either case, where condensation occurs on foreign substances, the nucleation is called ‘heterogeneous’ [12]. Then the word ‘nucleus’ refers to foreign particle that initiates the ice-phase. The size of the critical embryo varies from ten to one hundred molecules [18]. It is therefore, very important to know about the behaviour of small
dust particles, hygroscopic crystals and other naturally occurring nucleants as heterogeneous nuclei.

1.6.1 Nucleation on condensation nuclei

Let us consider aerosol particles which are wettable by water but completely water-insoluble. For the sake of simplicity it is useful to assume that a water embryo nucleated in super saturated vapour on a water-insoluble, partially wettable surface assumes the shape of a cap. Some experimental justification for the spherical cap assumption has been provided by Gretz [19]. Illustration for determining the volume, surface area and critical free energy of a spherical cap embryo of water (a) on a planar, water-insoluble, partially wettable substrate, (b) on a spherically convex, water-insoluble, partially wettable substrate and (c) on a spherically concave, water-insoluble, partially wettable substrate are shown in Figure 1.7.

1.6.2 Theory of heterogeneous ice nucleation on a planar substrate

The work is to determine the size of the critical embryo and critical free energy of cap shaped embryo on an insoluble aerosol particle surface. Let us first consider the simplest possible model for this process, and assume the surface on which the nucleation occurs is planar. Volmer [20] extended the original Volmer-Weber [21] nucleation theory to treat the case of condensation on a plane, solid surface. The geometry of a small droplet of liquid in contact with a solid surface can be characterized by two parameters. The cap shaped spherical droplet on a planar surface is as shown in the Figure 1.7 (a) and possesses two parameters (i) the radius of curvature of the spherical surface (r) and (ii) the angle of contact of the liquid on the
Figure 1.7 A spherical cap embryo of water:
(a) on a planar substrate
(b) on a spherically convex substrate and
(c) on a spherically concave substrate.
substrate (θ). The symbols L, S and V represent the liquid droplet, the catalysing substrate and the vapour respectively. When these three phases are in mutual mechanical equilibrium, the following relation holds good namely

\[ m = \cos \theta = (\sigma_{sv} - \sigma_{sl}) / \sigma_{LV} \]  \hspace{1cm} (1.1)

Here, the symbol \( \sigma \), in general, denotes the interfacial free energy per unit area between the respective phases, (represented by the symbols in the suffix).

If an embryo of this shape is formed from vapour the change in free energy (\( \Delta G \)) of the system can be expressed as,

\[ \Delta G = n_i (\mu_L - \mu_v) V_L + \sigma_{LV} A_{LV} + (\sigma_{SL} - \sigma_{SV}) A_{SL} \]  \hspace{1cm} (1.2)

which is a generalization of equation (1.1). where,

- \( n_i \) is the number of molecules per unit volume of the liquid,
- \( A \) is the surface area of the respective interfaces,
- \( \mu_L \) is the free energy of a single molecule in the liquid phase
- \( \mu_v \) is the free energy of a single molecule in the vapour phase and
- \( V_L \) is the volume of the liquid droplet.

If the radius of curvature of the liquid surface is \( r \) then the volumes and areas in terms of \( r \) and \( m \) are,

\[ A_{LV} = 2 \pi r^2 (1-m) \]
\[ A_{SL} = \pi r^2 (1-m^2) \] and
\[ V_L = \pi r^3 / 3 (2+m) (1+m)^2 \]  \hspace{1cm} (1.3)

The size of the critical embryo \( (r^*) \) can be determined when
Substituting equation 1.3 and 1.4 in equation 1.2, the change in critical free energy ($\Delta G^*$) can be found as

$$\Delta G^* = \frac{16\pi \sigma_{t,V} f(m)}{3[n_r KT \ln (p/p_0)]^2}$$

(1.5)

Since $-1 \leq m \leq 1$, the foreign surface has the general property of reducing the free energy necessary to form a critical embryo.

It is observed in the ice-water-vapour and in other systems that the occurrence of first nucleation is the most difficult process, as it requires high super saturation or supercooling. Even though the system is brought completely into the stability field of the parent phase between nucleation, a second nucleation is often easier.

### 1.6.3 General Equation

Fletcher suggested that the free energy of an embryo would be a minimum [22], when the shape of the embryo is polyhedron. We therefore assume that the embryo is a prismatic column of height 'h', inscribed radius ‘r’, containing n prism
faces as shown in Figure 1.8. If this embryo (L) forms from vapour phase (V) on a plane substrate (S), the increase in the free energy $\Delta G$ of the system is

$$\Delta G = \pi r^2 e h \Delta G_v + \pi r^2 e (\sigma_{sv} - \sigma_{sv}) + (\pi r^2 e + 2 \pi r e h) \sigma_{i,v} \quad (1.6)$$

Where $\Delta G_v$ is the free energy difference per unit volume of liquid phase between vapour phase and the embryo and

$$e = n/\pi \tan (\pi G/n) \quad (1.7)$$

If we now define a quantity, which is a measure of disparity between the ice embryo and substrate by

$$\gamma = (\sigma_{i,v} - \sigma_{sv} + \sigma_{sv}) / \sigma_{i,v} \quad (1.8)$$

then 1.6 can be simplified to

$$\Delta G = \pi r^2 e h \Delta G_v + \pi r^2 e \sigma_{i,v} + 2 \pi r e h \sigma_{i,v} \quad (1.9)$$

In a supersaturated parent phase $\Delta G$ is negative and $0 \leq v \leq 2$. Therefore, the value of $\Delta G$ increases initially with increase in $r$ and $h$, but after certain size is reached the ice embryo grows freely producing a decrease in the free energy of the system. The critical size of the embryo by applying the conditions

$$\frac{\delta \Delta G}{\delta h} = 0 \quad \text{and} \quad \frac{\delta \Delta G}{\delta r} = 0$$

leads to

$$r^* = \frac{2\sigma_{i,v}}{\Delta G_v} \quad (1.10)$$

$$h = r \gamma \quad (1.11)$$
Figure 1.8 A prismatic ice embryo growing upon a crystalline substrate $S$ from a parent phase $V$. 
and $\Delta G^* = \frac{4\pi\rho_0^3}{\Delta G_v^2}$

(1.12)

Where $r^*$ is the inscribed radius of the critical ice embryo and $\Delta G^*$ is the critical free energy. Equation 1.11 gives the equilibrium habit of the ice embryo. The shape of the crystalline nucleus has created great interest among many scientists [23-24].

1.7 ICE-FORMING NUCLEI OR FREEZING NUCLEI (IN)

Ice forming nuclei exhibit three basic modes of action. In the first, water is adsorbed directly from the vapour phase onto the surface of the IN where, at sufficiently low temperatures, the adsorbed water is transformed into ice. In the second mode, the IN initiates the ice phase from inside a supercooled water drop. In the third mode of action, the IN initiates the ice phase at the moment of contact with the supercooled drop. The first mode of action is called the deposition mode, and aerosol particles which exhibit this behaviour are called deposition IN; the second is called the freezing mode, and the corresponding AP are freezing nuclei; the third is called the contact mode, participated in by contact nuclei [11].

1.7.1 Characteristic Features of ice forming nuclei

a) Size Requirement:

The minimum size of nucleus which initiates the formation of ice crystals under different conditions of ice nucleation, is of particular interest. In general the nucleation efficiency should increase with the size of the nucleating particle. However when the size of the particle is very small there is large variation in the super cooling or super saturation required when there is a small change in the size of the nucleating particle.
Above a particular size the efficiency becomes almost constant; that is, no appreciable increase in the efficiency is observed when the size increases beyond a particular value. The critical size of the ice forming particles is the main objective of computations in the existing theories of nucleation [25].

b) Chemical Bond Requirement:

The chemical nature of an IN expressed in terms of the type and strength of the chemical bonds exhibited at its surface affects its nucleation behaviour. Ice crystal lattice is held together by hydrogen bonds (O-H-O) of specific strength and polarity [11]. The formation of a weak hydrogen bond between water molecules and the surface of nucleus is necessary for high nucleating ability. Any occurrence of a strong co-ordination bond decreases such an ability [26]. Fukuta [27] found that a hydrogen bonding molecule at the surface of the nucleus should also have a rotational symmetry.

c) Active-Requirement:

Ice-nucleation is a very localized phenomenon in that it proceeds at distinct active sites on a substrate [11]. An active site may be

i. a morphological surface inhomogeneity such as a step, crack or cavity at the surface,

ii. a chemical inhomogeneity generally caused by a foreign atom or ion which is relatively hydrophobic with respect to the rest of the surface or

iii. an electrical inhomogeneity other than ions on the surface [11].

The effectiveness of topographic surface features to initiate ice phase from vapour has been given by Bryant et al [28], who studied the ice nucleating properties of CuS in the depositional mode. Photographs taken during the course of these studies revealed that ice crystals appear preferentially at cleavage and growth steps, at
cracks, and in cavities, and at the edges of the substrate surface (see plate 1.a). The result is supported by the present work which shows that the ice nucleability of a ferroelectric substrate BST single crystal surface could be improved by etching, ie, "channel type" etch pit of ferroelectric domains enhances the ice nucleation (see plate 1.b).

d) Crystallographic Requirement:

The geometrical arrangement of bonds at the substrate surface is often of equal or greater importance than their chemical nature. Since ice nucleation on a foreign substrate may be regarded as an oriented (or epitaxial) overgrowth of ice on this substrate, it is quite reasonable to assume that this overgrowth is facilitated by having atoms, ions or molecules which are as close as possible to that of water molecules in some low index plane of ice [11]. An example of the crystallographic matching between the (0001) planes of ice and CuS is shown in Figure 1.9 and the Figure 1.10 shows the similarities between the pattern of the split mica plane and the pattern of the base plane of an ice crystal.

1.8 ICE NUCLEATION OF SILVER IODIDE

The ice-nucleating properties of silver iodide were discovered by Vonnegut (1947), and since than it has remained the pre-eminent nucleating agent in this field [29]. Other substances such as lead iodide and cuprous oxide have occasionally been proposed as more efficient nucleating agents, but their claims have not been generally substantiated [30-31].
a) An epitaxial deposit of ice crystal at the steps of a hexagonal growth spiral on cadmium iodide.

b) Location of ice crystals appear at the channel type etch pattern on Barium Strontium Titanate.
Figure 1.9 Relative atomic position in the (0001) plane of CuS and ice. • Cu atoms. ○ H₂O molecules.

Figure 1.10 (a) Lattice structure of mica plane (b) Basal plane of ice crystal.
1.8.1 Structure of Silver iodide

Silver iodide is generally considered to exist in three solid forms [32]. Their properties are briefly as follows:

\( \alpha - \text{AgI} \) is the stable form between 146°C and the melting point, 555°C. It is dark brown in colour and is cubic in structure, the iodine atoms occupying a body-centred cubic lattice with separations of 2.18 Å. The silver atoms are not uniquely positioned but are distributed statistically over the thirty largest spaces in the iodine lattice. On cooling below 146°C the \( \beta \)-modification is produced spontaneously.

\( \beta - \text{AgI} \) is the stable form between 137°C and 146°C, though it commonly exists in a metastable state below this range. It is greenish-yellow in colour and hexagonal in form. The atoms form an almost exact wurtzite structure at low temperature (-180°C), but at ordinary temperatures there is probably a random distribution of silver atoms in four positions which surround tetrahedrally the ideal wurtzite positions [33].

\( \gamma - \text{AgI} \), which has cubic zincblende structure, is generally thought to be the stable form below 137°C. The only difference between \( \beta \)- and \( \gamma \)- form is that the \( \beta \)-form has a layer structure ABABAB…, while the \( \gamma \)-form is stacked in order ABCABC…, From the X-ray viewpoint at least then, a small concentration of \( \gamma \) and \( \beta \) is indistinguishable from stacking faults. The lattice constants of the three forms are shown in Table 1.1.
Table 1.1. 
Crystallographic data for AgI

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature range in (°C)</th>
<th>unit dimension a₀ in (Å)</th>
<th>Crystal form</th>
<th>Molecules per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>α - AgI</td>
<td>146-555</td>
<td>5.034</td>
<td>cubic</td>
<td>2</td>
</tr>
<tr>
<td>β - AgI</td>
<td>137-146</td>
<td>4.580</td>
<td>hexagonal</td>
<td>2</td>
</tr>
<tr>
<td>γ - AgI</td>
<td>&lt;137</td>
<td>6.470</td>
<td>cubic</td>
<td>4</td>
</tr>
<tr>
<td>Ice</td>
<td>0.0</td>
<td>4.52</td>
<td>hexagonal</td>
<td>4</td>
</tr>
</tbody>
</table>
1.9 EPITAXIAL GROWTH ON SINGLE CRYSTAL SUBSTRATE

Epitaxy is the process for growing regularly oriented, thin films on a substrate. Ice nucleation on a foreign substrate may be regarded as an oriented (or epitaxial) overgrowth of ice on this substrate. Because of the geometric regularity of molecular positions in crystals, the surface and interfacial energies of crystals are always expected to be anisotropic [33]. Thus $\sigma_{LV}$, $\sigma_{SV}$, $\sigma_{SL}$, and contact angles $\theta$ are all functions of crystal orientation. Particularly, the interfacial energy between ice and substrate is a function of relative orientation of ice and substrate and of the orientation of the interface plane.

In fact AgI has been found explicitly seeking epitaxial relations [29], having a reasonably good lattice fit with ice. The close resemblance between the structure of ice, lead iodide and silver iodide is shown in the Figure 1.11 drawn approximately to scale.

1.10 LATTICE MISFIT AND STRAIN ENERGY

The lattice parameter of AgI, though very close to that of ice is not exactly equal to that of ice. There is a certain amount of misfit between AgI and ice lattices. This mismatch or misfit is also called disregistry and is given by

$$\delta = \left| \frac{a_i - a_0}{a_0} \right|$$

where $a_i$ is the crystallographic lattice parameter of particular face of the nucleus, $a_0$ is the corresponding constant in the ice lattice. Assuming the embryo can be strained by an amount $\varepsilon = \left( \frac{a_i - a_0}{a_0} \right)$, where $a_0$ and $a_i$ are the lattice parameters of ice in the
Figure 1.11 Models of the crystal structures of ice, lead iodide and silver iodide. In the latter white spheres are iodide ions and black spheres metallic ions.
strain-free and the strained conditions, respectively, and assuming the substrate strain is negligible, the actual crystallographic misfit between the embryo and particular face of the IN is given by $\delta - \varepsilon$. If $\delta = \varepsilon$ the embryo fits the surface element of the IN coherently. If the ice embryo cannot be strained by the full amount, then $\delta - \varepsilon > 0$ and the ice embryo joins IN incoherently.

1.11 LATTICE MATCHING

From the above discussion it is clear that any ice nucleator must have the lattice strain as low as possible. Fletcher [34] has treated an one-dimensional case. Figure 1.12 shows several possible types of lattice matching between the basal plane of ice and the substrate surface. In the figure the small circles show the positions of water molecules in ice and large circles are surface atoms or molecules of the substrate.

The effect of the crystallographic properties of IN on ice nucleation has been studied by a large number of investigators [35]. Some selected results of these studies are summarised in Table 1.2, where the threshold temperature for ice nucleation in the deposition mode is listed for various chemical compounds as a function of their crystallographic characteristics. The substances listed in table 1.2 seem to derive their warm ice nucleation threshold from a close fit of their crystal lattice to that of ice. An unequivocal proof of the necessity, although not for good ice nucleability was given by Evans [36]. However, despite the obvious importance of the crystallographic properties of a substrate to its nucleability, Table 1.2 demonstrates clearly that no unique correlation can be established between ice nucleation threshold and any of the
Figure 1.12: Types of lattice matching between basal plane of ice and substrate surface.
crystallographic characteristics such as symmetry or misfit. The main reason for this behaviour is the role played by active sites, which is discussed in the eighth chapter.

Table 1.2

Crystallographic misfit between various chemical compounds and ice, and its relation to the nucleability of these compounds.

<table>
<thead>
<tr>
<th>Chemical compounds</th>
<th>Lattice constants (Å)</th>
<th>Ice Matching Plane</th>
<th>Misfit between substrate and ice (°C)</th>
<th>Approx. ice nucleation threshold (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice -Ih</td>
<td>D''hex</td>
<td>a₀ = 4.520</td>
<td>prism (0001) + 8.1 (1:1)</td>
<td>-3 to -6</td>
</tr>
<tr>
<td>β -A₄ I</td>
<td>C''hex</td>
<td>b₀ = 7.360</td>
<td>(0001) basal (1010) + 1.5 (1:1)</td>
<td>-3 to -6</td>
</tr>
<tr>
<td>γ - A₄ I</td>
<td>T₄ cubic</td>
<td>c₀ = 4.592</td>
<td>prism (111) basal (1210) + 1.5 (1:1)</td>
<td>-3 to -6</td>
</tr>
<tr>
<td>MgTe</td>
<td>C''hex</td>
<td>a₀ = 4.520</td>
<td>(0001) basal (1010) + 0.4 (1:1)</td>
<td>-4 to -5</td>
</tr>
<tr>
<td>PbI₂</td>
<td>D''trig</td>
<td>b₀ = 7.510</td>
<td>(111) basal (1210) -0.4 (1:1)</td>
<td>-4 to -7</td>
</tr>
<tr>
<td>HgTe</td>
<td>T₄ cubic</td>
<td>c₀ = 4.520</td>
<td>(0001) basal (1010) -0.2 (1:1)</td>
<td>-4 to -6</td>
</tr>
<tr>
<td>CdTe</td>
<td>T₄ cubic</td>
<td>a₀ = 6.496</td>
<td>(111) basal (1210) -11.5 (1:1)</td>
<td>-5 to -12</td>
</tr>
<tr>
<td>CuI</td>
<td>T₄ cubic</td>
<td>b₀ = 6.41</td>
<td>(111) basal (1210) -5.5 (1:1)</td>
<td>-4 to -7</td>
</tr>
<tr>
<td>CuS</td>
<td>D''hex</td>
<td>c₀ = 6.04</td>
<td>(111) basal (1210) -9.5 (1:1)</td>
<td>-4 to -8</td>
</tr>
<tr>
<td>Ag₃S</td>
<td>C''mono</td>
<td>a₀ = 3.80</td>
<td>(0001) basal (1010) -2.8 (1:1)</td>
<td>-4 to -9</td>
</tr>
<tr>
<td>HgI₅</td>
<td>C''ortho</td>
<td>b₀ = 4.20</td>
<td>(0101) basal (1210) -7.1 (1:1)</td>
<td>-5 to -8</td>
</tr>
<tr>
<td>CdSe</td>
<td>C''hex</td>
<td>c₀ = 4.67</td>
<td>(0101) basal (1210) + 3.3 (1:1)</td>
<td>-5 to -8</td>
</tr>
<tr>
<td>ZnSe</td>
<td>T₄ cubic</td>
<td>a₀ = 6.93</td>
<td>(0101) basal (1210) -11.5 (1:1)</td>
<td>-5 to -12</td>
</tr>
</tbody>
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