TOWARD THE MEASUREMENT OF RELIABLE GRAIN-BOUNDARY DIFFUSION COEFFICIENTS IN OXIDES

by

YONG-CHAE CHUNG

B.S. Inorganic Materials Engineering
Seoul National University (1988)

M.S. Inorganic Materials Engineering
Seoul National University (1990)

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Signature of Author

Certified by

Bernhardt J. Wuensch
Professor of Ceramics
Thesis Supervisor

Accepted by

Carl V. Thompson II
Professor of Electronic Materials
Chair, Departmental Committee on
Graduate Students

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ABSTRACT

A Chemical Vapor Transport (CVT) method was successfully used to grow NiO bicrystals using single crystals of MgO as substrates. The most favorable growth conditions were obtained at 1400K using 250 torr of HCl as a carrying agent. At this condition a growth rate of over 100 µm/hr was easily achieved. The CVT-grown NiO bicrystals commonly displayed facets. The grain boundary in the bicrystals was observed to be perpendicular to (001) growth surface. The high reflectivity of the facets along the growth direction in the bicrystals suggest high mechanical quality. The CVT-grown NiO crystals were easily detached from the MgO substrate by dissolving away the latter in 85% H3PO4 at 190°C. Using these free standing NiO crystals, the single-crystal epitaxial state of the deposits and their impurity contents were determined. The concentration of cation impurities and Cl content in the CVT-grown crystals were investigated by ICP (Inductively Coupled Plasma) mass-spectrometric analysis and neutron activation analysis, respectively. High-resolution transmission electron microscopy of a Σ13 (510) boundary revealed a structure at the atomic scale that provided no evidence for segregated phases.

To obtain a grain-boundary diffusion coefficient from a diffusion depth profile, Le Claire's method had generally been used in most grain-boundary diffusion experiments. However, from a numerical assessment of the accuracy, Le Claire's method was shown to create errors of as large as 70% in determining a grain-boundary diffusion coefficient from a diffusion depth profile in the useful ranges of experimental conditions that provide a detectable amount of diffusant distinguishable from the background concentration. A new and greatly-improved expression that permits determination of an accurate grain boundary diffusion coefficient within 1% error for the entire feasible experimental range of grain boundary diffusion experiments was developed by numerical computations.
The contribution of a space charge region to grain boundary diffusion was quantitatively investigated by solving a two-dimensional diffusion equation with a position-dependent diffusion coefficient. The Finite Difference Method was carefully applied to this complicated 2-dimensional diffusion equation with a study of the effect of grid size and time step size on the result of the computation. In a range where \( \frac{z e \Phi_\infty}{kT} \) varied from 1.5 to 5, the computed value of \( \beta \left( = \frac{D_{gb}}{D_{bulk}} - 1 \right) \frac{a}{\delta} \) varied from 0.67 to 8.54; \( \beta \) is the quantity directly related to the amount of enhancement of grain-boundary diffusivity relative to bulk diffusivity. Using this result, the contribution of a space charge region to grain boundary diffusion can be easily calculated once a potential at the bulk and a dielectric constant are determined.

As a part of an attempt to solve the diffusion equation with complex boundary conditions and an initial condition, the Finite Difference Method of numerical analysis was applied to solve a one-dimensional diffusion equation which has a concentration-independent diffusion coefficient. With various conditions of \( \lambda \left( = \frac{D \Delta t}{\Delta x^2} \right) \), \( 0.001 \leq \lambda \leq 0.4 \), the Forward-Difference method and the Crank-Nicolson method were applied to the diffusion equation. By monitoring the error between the analytic solution and the numerical solution, it was confirmed that, at a very specific condition when \( \lambda \) is \( 1/6 \), the Forward-Difference method yields an extremely accurate result. The atomistic description of diffusion successfully provides a physical basis for the reason why there should be no significant error at a \( \lambda \) value of \( 1/6 \) in the Forward-Difference method. It was recognized that the Forward-Difference method actually simulates the atomistic diffusion in certain media at this value of \( \lambda \).

Thesis Supervisor: Bernhardt J. Wuensch
Title: Professor of Ceramics
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Chapter I

Introduction

A grain boundary has special properties quite different from bulk material and their presence in a material causes many significant changes in, for example, mechanical behavior and electrical properties. These changes are significant as the great majority of materials employed in technology are polycrystalline. Consequently, study of the nature of grain boundaries has been a major area of materials research.

There have been many studies concerning the grain boundary. However, a complete understanding of structure - property relations for the grain boundary has not yet been achieved. The first reason for this is because the structure of grain boundary is not simple as that of the bulk. The structure of the grain boundary is that of two-dimensional interface, perhaps as little as a few atomic layers in thickness, which makes difficult the specification of its structure. The second reason is that many factors can make it difficult to study the inherent effects of the grain boundary. In oxides there is grain boundary potential as well as structural misfit on the grain boundary. This causes defect concentration gradients and a space charge region adjacent to the grain boundary[1-8]. Consequently, the grain boundary provides excellent sites for impurity segregation and precipitation which can mask intrinsic behavior completely.
One of the interesting properties that is related to a grain boundary in an oxide system is that of oxygen self diffusion along grain boundaries which usually dominates the process of sintering and creep, etc. Many studies reported enhanced diffusion along grain boundaries compared to bulk diffusion, although most of them are about cation diffusion not oxygen diffusion along grain boundaries[9-14]. However, the details of the origin of grain boundary diffusion could not be revealed because of the complexity arising from variations of structure and the space charge region created by the grain boundary potential, as mentioned earlier[15-20]. To systematically investigate oxygen diffusion along a grain boundary, we need at first a simple grain boundary which has a well-defined structure. To see the intrinsic properties of a grain boundary, the impurity level in the crystal and at the boundary should be lower than the intrinsic defect concentration. We also need some precise formalism for obtaining a grain boundary diffusion coefficient from an accurate experimental measurement of a diffusion depth profile. Secondary Ion Mass Spectroscopy (SIMS), provided the analysis can be performed with high lateral resolution, has recently provided a means for acquiring such data. The diffusion equation for grain boundary diffusion is complicated in the sense that it is two-dimensional and there are two different diffusion coefficients, a bulk diffusion coefficient and a grain boundary diffusion coefficient. There is no exact analytical way of extracting a grain boundary diffusivity from an experimental diffusion depth profile. There only exist several approximate ways[21-34]. But their accuracy is hardly known. To separate the structural influence of the grain boundary from the effect of the grain boundary potential, it is necessary to fabricate a bicrystal which is controlled by only one of the two factors, that is either grain boundary structure alone or only the grain boundary potential. However, it
has thus far been impossible to make such crystals to experimentally achieve our goal.

This study started from these above considerations. In Chapter II, the fabrication of oxide bicrystals having special boundaries with high purity is described. NiO is chosen as a system for this study from the following reasons: (1) It has the simple rock salt structure, which is well understood and has been successfully modeled for monovalent compounds. (2) The defect structure of NiO has been understood quite well compared to other oxides theoretically and experimentally[35-52]. (3) The structures of grain boundaries of NiO have been studied extensively by both experiments and modelings[53-66]. (4) Since it is a nonstoichiometric oxide, the defect structure of grain boundary can thus, in principle, be controlled through variation of oxygen partial pressure. (5) There have been not many grain boundary diffusion experiments in NiO: Most of them were about grain boundary diffusion of cations[67-71]. Chen and Peterson[67] found an enhanced diffusion of Co and Cr along grain boundaries using polycrystalline samples and bicrystals. The temperature dependence of grain boundary diffusivity product(grain boundary width times grain-boundary diffusivity) was about the same as that of bulk diffusivity. However, they couldn't detect any oxygen partial pressure dependence and structure dependence within experimental error. Atkinson and Taylor et al.[68-70] have measured the diffusion of Ni, Co, Cr, and Ce along grain boundaries in polycrystalline samples and bicrystals. Concerning Co[69] and Cr[70], their data was not compatible with that of Chen and Peterson[67]. In fact, the measured grain boundary diffusivity was almost two orders of magnitude lower than that of Chen and Peterson[67]. In fact, the activation energies of grain boundary diffusion for two cases, Co and Cr, respectively. Also the activation energies of grain boundary diffusion for two cases, Co and Cr, were less than
that of bulk diffusion, which is a contradiction to the observation of Chen and Peterson[67]. They found a dependence of oxygen partial pressure on the grain boundary diffusivity for Cr, which is also contradictory to Chen and Peterson[67]. It is truly interesting to note that a more recent experiment[71] could not find any enhanced diffusion of Co along grain boundaries in a NiO bicrystal within experimental error. They described the reason for no difference in terms of the lower sensitivity and resolution of the electron microprobe analysis technique, and the possible influence of impurities. Compared to cation diffusion, there has been only one study of oxygen self diffusion along grain boundaries in NiO and this used poly-crystalline samples not bicrystals[72]. (6) NiO is an oxide that has properties that make it ideally suited to analysis by SIMS. As the material has appreciable electronic conductivity, charge accumulation during bombardment with the primary ion beam is not serious compared to insulating stoichiometric oxides such as MgO that have been previously studied in this laboratory. Moreover, the largest source of error in the determination of diffusion coefficients for MgO was the uncertainty in the calibration of sputtering depth with sputtering time. This was due to the ease with which MgO hydrates upon exposure to air. Measurement of the depth of the sputtered pits was difficult as they were quickly obliterated by the formation of layer of brucite, Mg(OH)2. Nickel oxide does not possess this tendency to hydrate. The above consideration tells us that NiO bicrystal which has high purity and simple-special structure, which will be grown in this study, can truly provide reliable grain boundary diffusivity. This reliable grain boundary diffusivity can solve the controversial issues in the amount enhancement of diffusivity along grain boundaries. And also the defect structure of the grain boundary
which might be possibly controlled by the oxygen partial pressure can be determined using these bicrystals.

Chapter III presents a new method for obtaining, with greatly improved accuracy, an oxygen grain-boundary diffusion coefficient from a measured diffusion depth profile. The accuracy of existing methods is completely reviewed for the experimentally meaningful range of annealing experiments for diffusion. Such conditions are those that give detectable amounts of diffusant separable from the background level. Numerical integration is used to evaluate the integral form of the exact solution of the grain boundary diffusion equation under conditions of constant surface concentration - the boundary conditions likely to be applicable for most experimental studies of oxygen migration. From the calculation a very accurate way of obtaining grain boundary diffusion coefficients (within 1% relative error) can be achieved.

Chapter IV focuses on the effect of a space charge region on the enhanced diffusion. As an attempt to separate the charge effect of a grain boundary from a structural influence, a calculation is performed for a virtual diffusion experiment in which the sample has only a space charge region and no structural misfit. A numerical method is applied to solve the two-dimensional diffusion equation with a diffusion coefficient which varies continuously with distance from the boundary. After careful consideration of the effects of the grid size and time step size, a diffusion depth profile is obtained for various grain boundary potentials. Using the approximation technique that is established in Chapter III, a relation between enhanced diffusion and grain boundary potential can be obtained. From this relationship the effect of space charge region on the enhanced diffusion, which can be expressed as grain boundary diffusion coefficient, can be easily calculated provided that the potential at the bulk and the dielectric constant of
the material are known. In Chapter V, a rather interesting topic is discussed. Finite Difference Methods are applied to the calculation of bulk diffusion gradients, for which the analytical solution is already known. The accuracy of the Finite Difference Methods is investigated completely for a range of conditions, and a strong case is established for the superiority of the Forward-Difference method when it is performed with specific computational parameters. A physical explanation is suggested for this high-degree of computational accuracy by comparing the steps in the computational method with the mechanism of atomic migration. A summary of the thesis and suggestions for future work are given in Chapter VI.
Chapter II

Epitaxial Growth of NiO Bicrystals via Chemical Vapor Transport

2.1 Introduction

In oxides, the transport properties, including diffusion, are governed by the ionic defect concentrations: metal vacancies, metal interstitials, oxygen vacancies, or oxygen interstitial concentration as well as possible defect complexes. To study intrinsic transport properties it is absolutely necessary to use an ultra pure crystal which has impurity levels lower than its own intrinsic defect concentration. Otherwise, only extrinsic properties can be observed. To see intrinsic effects of grain boundaries in polycrystalline material is much harder than to observing intrinsic effects in single crystal material. Even if the overall impurity level is lower than the intrinsic defect concentration, the possibility of impurity segregation around the grain boundary, due to the grain boundary potential, can mask intrinsic properties. Another factor which makes it difficult to study the intrinsic properties of a boundary is the complexity of its structure, as discussed in Chapter I. Fabrication of isolated grain boundaries free of segregated impurity and with selected and specific orientation of the adjoining single crystal regions is an essential part of a study in any attempt to establish fundamental structure-property relationship for such interfaces.
Chemical Vapor Transport (CVT) methods have proved to be a very effective means for growth of high-purity single crystals, as thermodynamics favors preferential transport of only specific elements from the source material to the substrate[73-88]. A very effective apparatus for the growth of MgO by transport with HCl as a carrying agent was developed by Gruber[77]. This process was adapted in this laboratory to the growth of epitaxial Mg\textsuperscript{18}O isotopic bicrystal layers on MgO bicrystals which had been prepared by a hot pressing method[78]. This method has advantages for the growth of high-purity oxide specimens compared with growth from the liquid. The source material is kept separated from the grown material during the growth run, and growth is accomplished in a relatively short period of time at a temperature far below the melting point of the oxide. This, in turn, greatly reduces the possibility of the diffusion of impurities to the grain boundary during growth and, similarly, results in negligible interdiffusion between the deposited crystal and the substrate, a feature especially important in heteroepitaxial growth.

In this study, the CVT procedure for transport with HCl(g) was extended to NiO for the purpose of growing bicrystals with grain boundaries of high purity and controlled orientation as well as high purity single crystals. A unique feature of this heteroepitaxial NiO growth is that it proved possible to dissolve the substrate material to produce free-standing single crystals or bicrystals. This facilitated characterization of the CVT-grown crystals to check the crystallinity and the purity. Also, these free-standing single and bicrystals are suitable for the later study of intrinsic properties of the grown crystals without the possibility of contamination from the substrate.
2.2 Experimental Procedure

2.2.1 Substrate preparation

Single crystals of MgO, readily available from commercial sources (Advanced Composite Materials; Greer, SC), were used as substrates for the CVT growth of NiO single crystals and bicrystals. Since there is only 1% difference in lattice constant for these isostructural materials, epitaxial growth seemed likely to occur and the introduction of dislocations due to lattice mismatch would be minimal. For growth of single crystals of NiO, (100) MgO single crystal plates with dimensions of 13 × 13 × 1 mm were used as substrates. The preparation of the MgO substrates for bicrystal growth is somewhat complicated. Figure 2.1 illustrates the technique used to prepare the MgO substrates for bicrystal growth. Two MgO single crystals were cut with the desired tilt orientation to (100), half of 36.87° for Σ5 (310) or one-half 22.62° for Σ13 (510) [89-104]. The surfaces to be joined were polished in several steps down to 0.3 μm diamond paste. The dislocations introduced during the polishing step were removed by chemical etching in 85% H₃PO₄ solution for 2 minutes at 120°C. The chemical etching procedure is completely illustrated elsewhere [105]. The two seed crystals were tightly bound with Pt wire, taking care to keep the desired tilt orientation without introduction of a twist component. The fact, as noted above, that the MgO substrate may subsequently be removed permits the fabrication of a mechanically-robust specimen in which a relatively-thin epitaxial layer no longer resides on a thick unbonded substrate. This, in turn, avoids the need for hot-pressing a bicrystal substrate. Such a step involves elevated temperatures and
Fig. 2.1  Schematic illustration of the preparation of a MgO substrate for fabrication of NiO bicrystals.
pressures, processing conditions that invite impurity segregation at the substrate grain boundary. This could result in boundary diffusion of the impurity into the epitaxial boundary during growth.

2.2.2 CVT process for NiO growth

When HCl(g) is used as a carrying agent, the required reaction for the CVT process of transporting NiO(s) is as follows:

\[
\text{NiO}(s) + 2\text{HCl}(g) \leftrightarrow \text{NiCl}_2(g) + \text{H}_2\text{O}(g) \quad (2.1).
\]

The basic idea behind the CVT method is simple: According to thermodynamics, if the forward reaction of (2.1) and the reverse reaction of (2.1) are favorable at the source pellet and the substrate crystal, respectively, NiO(s) will be transported from the source to the substrate in what amounts to a chemically-assisted vaporization-condensation reaction. Nickel Oxide powder (NiO, 99.998%, Johnson Matthey, Ward Hill, MA) was cold pressed into a pellet, which was used as a source material. The NiO source pellet was then placed inside of a quartz ring upon which the prepared MgO substrates were placed (Fig. 2.2). The Pt ring employed in the arrangement originally used by Gruber[77] was replaced by high-purity quartz glass in the present work. It was found that the ring had low electrical conductivity and was not heated by induction. This permitted better control of the temperature gradient and
Fig. 2.2 Schematic illustration of the way to install the MgO substrate on a quartz ring for the growth of (a) single crystals, and (b) bicrystals of NiO.
resulted in improved growth. The Pt binding wires which belonged to the substrate for bicrystal growth, were positioned outside the limits of the area on which epitaxial growth was to occur. A typical separation between MgO substrate and NiO source pellet was ~2mm. Since the temperature difference between the source and the substrate is a very important factor in the CVT process, an RF heating furnace was used to provide a sufficient temperature difference between them. By careful positioning of the induction coils relative to the Pt crucible in which the MgO substrate and the NiO source pellet had been placed, a sufficient temperature difference between the source pellet and the substrate was easily obtained (Fig. 2.3).

The CVT process for NiO growth was performed by several steps. Firstly, the growth chamber was evacuated down to $10^{-6}$ torr using a mechanical pump, a diffusion pump, and several steps of nitrogen gas purging process. At this stage, several proper bake out steps at ~800°C were necessary to obtain a good vacuum. After attaining a sufficient degree of vacuum, a specific amount of HCl gas was introduced to the growth chamber and the growth chamber was heated instantly to the growth temperature by the RF heating coil. The growth chamber was maintained as a closed system while growth run was in progress, usually for several hours.
Fig. 2.3 Schematic diagram of the apparatus used to grow NiO crystals.
A: quartz chamber   B: Pt wire support
C: Pt foil crucible cover  D: Pt crucible
E: MgO substrate  F: epitaxial deposit of NiO crystal
G: high purity quartz ring  H: source NiO
I: RF heating coil
2.3 Results and Discussion

2.3.1 Thermodynamics of NiO growth by CVT

In the CVT process of NiO growth, three steps are involved to transport NiO from the source material to the MgO substrate; (I) At the source, NiO(s) reacts with HCl(g) and has to be transformed to NiCl$_2$(g) and H$_2$O(g) (the forward direction of the reaction (2.1)), (II) These two gaseous species, NiCl$_2$(g) and H$_2$O(g), diffuse to the substrate, (III) At the substrate, NiCl$_2$(g) and H$_2$O(g) react with each other and transform to NiO(s) and HCl(g) (the reverse direction of the reaction (2.1)). Figure 2.4 illustrates these 3 steps schematically. Since the distance between the source pellet and the substrate is only 2mm in our system, the kinetics of step (II) can be considered as a minor factor compared to those of steps (I) and (III). This means that if step (I) and step (III) can happen favorably at the source and the substrate, respectively, NiO can be transported to the MgO substrate from the source pellet. It is well known that Gibbs energy difference between products and reactants determines the possibility of the occurrence of a reaction. For the reaction (2.1) Gibbs energy change, $\Delta G$, can be expressed as

$$
\Delta G = \Delta G^0(T) + RT \ln \left( \frac{P_{NiCl_2} \cdot P_{H_2O}}{P_{HCl}^2} \right)
$$

(2.2)

where $\Delta G^0$ is the standard Gibbs energy change of the reaction (2.1), (Fig. 2.5), $P_i$ is the partial pressure of gaseous species $i$, $T$ is the absolute temperature, and $R$ is the gas constant.
Fig. 2.4 Schematic diagram of the CVT process for NiO(s) transport from source to substrate via HCl(g).
Fig. 2.5 Standard Gibbs energy change for reaction (2.1), which was calculated using data of [106].
To transport NiO from the source to the substrate by the CVT process, the conditions should be such that $\Delta G < 0$ at the source and $\Delta G > 0$ at the substrate. At the initial stage of the CVT process of NiO growth, there is only one gaseous species, HCl(g), in the closed system. This means that initially $\Delta G$ is minus infinity at the growth temperature and NiCl$_2$(g) and H$_2$O(g) can be produced at the source. This reaction proceeds until equilibrium is obtained. The equilibrium partial pressure of three gaseous species of the reaction (2.1) can be decided by reaction thermodynamics as

$$P_{NiCl_2,eq} = P_{H_2O,eq} = \frac{K}{1 + 2K} P_{HCl,init}$$

$$P_{HCl,eq} = \left(1 - \frac{2K}{1 + 2K}\right) P_{HCl,init}$$

where $K = \exp\left(-\frac{\Delta G^\circ}{2RT}\right)$, and $P_{HCl,init}$ is the initial amount of HCl gas, and $P_{i,eq}$ is the equilibrium partial pressure of gaseous species $i$.

For the CVT process of NiO growth to occur, $P_{NiCl_2,eq}$ at the source should be larger than $P_{NiCl_2,eq}$ at the substrate. The equilibrium partial pressure difference between them, $\Delta P$, can be expressed as follows if the temperature of the source is $T_1$ and the temperature of the substrate is $T_2$:

$$\Delta P = \left(\frac{K_1}{1 + 2K_1} - \frac{K_2}{1 + 2K_2}\right) P_{HCl,init}$$

where $K_1 = \exp\left(-\frac{\Delta G^\circ(T_1)}{2RT_1}\right)$ and $K_2 = \exp\left(-\frac{\Delta G^\circ(T_2)}{2RT_2}\right)$.

For $\Delta P$ to be positive,
\[ \Delta H^\circ \left( \frac{1}{T_1} - \frac{1}{T_2} \right) < 0 \]  \hspace{1cm} (2.5) 

where \( \Delta H^\circ \) is the standard enthalpy change for the reaction (2.1) which can be assumed to be independent of temperature. From Fig. 2.5, it is evident that \( \Delta H^\circ \) is positive. Consequently, the temperature of the source \( T_1 \) should be higher than the temperature of the substrate \( T_2 \) to satisfy the requirement of Eqn. (2.5). The equilibrium partial pressure difference, \( \Delta P \), can be considered as a driving force for the CVT process of NiO growth since the NiO growth on the substrate is a process of Langmuir evaporation and condensation[107] for which flux \( J \) can be expressed as

\[ J = \frac{\Delta P}{\sqrt{2 \pi n m k T}} \]  \hspace{1cm} (2.6) 

where \( m \) is the molecular weight of NiCl\(_2\), and \( k \) is the Boltzmann constant.

The total pressure of the CVT system, \( P_{tot.} \), was monitored as a function of time during the NiO growth. Figure 2.6 shows the result for a case where the growth temperature was 1400K (the temperature of the source) and the initial HCl pressure was 250 torr. As may be seen, total pressure decreased as time passed. If the reaction (2.1) is completely reversible at the source and the substrate respectively, there should be no total pressure decrease in the growth chamber. This means that at the substrate NiCl\(_2\)(g) and H\(_2\)O(g) could not react fully with each other to grow NiO crystal and release HCl(g). These extra gaseous species, NiCl\(_2\)(g) and H\(_2\)O(g), were simply deposited as some form of NiCl\(_2\) and H\(_2\)O on the chamber wall, which was maintained at relatively low temperature. This resulted in a decrease of the total pressure, which is dominated by gaseous species. The driving force for the CVT process of NiO
Fig. 2.6 Monitoring of the total pressure in the crystal growth chamber during crystal growth.
growth, $\Delta P$, of Eqn. (2.4) can be calculated from the results of monitoring the total pressure (Fig. 2.6) if one assumes a temperature for the substrate. Taking this as 1350K, and reasonably assuming that the measured $P_{tot.}$ is the same as $P_{HCl,init.}$, Eqn. (2.4) becomes

$$\Delta P = \left( \frac{K_1}{1 + 2K_1} - \frac{K_2}{1 + 2K_2} \right) P_{tot.}$$

(2.7).

As may be seen in Fig. 2.7, $\Delta P$, decreased exponentially as time passed. Here the substrate temperature was assumed to be 1350K because of the experimental difficulty in measuring the temperature of the substrate accurately. This means that the result of the calculation of $\Delta P$ for Fig. 2.7 is not absolute, but rather an arbitrarily scaled value because of the approximate value of $K_2$ in the term in parenthesis on the right of Eqn. (2.7). However, Fig. 2.7 can give enough information about the change of the driving force for the CVT process of NiO growth.

One more thing to be considered for the CVT process of NiO growth is the possibility of the presence of liquid phase or solid phase NiCl$_2$ instead of NiCl$_2$(g) when NiO(s) reacts with HCl(g). In other words,

$$\text{NiO(s) + 2HCl(g) } \Leftrightarrow \text{NiCl}_2(s) + \text{H}_2\text{O(g)}$$  (2.8),

$$\text{NiO(s) + 2HCl(g) } \Leftrightarrow \text{NiCl}_2(l) + \text{H}_2\text{O(g)}$$  (2.9).

These two reactions should be avoided to grow NiO crystal effectively. If these two reactions happen, NiCl$_2(s)$ and NiCl$_2(l)$ just simply remain in the NiO pellet and are not available to grow NiO crystal. This results in a loss of NiO(s) and HCl(g). In Fig. 2.8 the standard Gibbs energy difference between products and
Fig. 2.7 The change of equilibrium partial pressure difference between source and substrate, the $\Delta P (=P_1-P_2)$, during crystal growth assuming that the temperature of the substrate is 1350K and the temperature of the source pellet is 1400K.
Fig. 2.8 Standard Gibbs energy change for reactions (2.1), (2.8), and (2.9), which were calculated using data of [106] showing that the CVT process should be operated above 1250K to grow NiO effectively.
reactants for the reactions (2.8) and (2.9) is calculated[106] and compared with Fig. 2.5. It is evident that the CVT process of NiO growth should be carried out above 1250K to avoid the possibility that NiO(s) simply transforms to NiCl₂(s) and NiCl₂(l) instead of making NiCl₂(g).

Jeffes[74] suggested that to achieve a high transport rate the CVT process has to be performed around the temperature at which the standard Gibbs energy difference between products and reactants is close to 0, which is ~1750K for NiO case. However, the higher the growth temperature, the higher the possibility of impurity segregation around the grain boundary during bicrystal growth as well as interdiffusion between the deposited NiO crystals and the substrate MgO crystals. To avoid such possibilities, the low temperature range of 1250-1500K using 30 to 300 torr of initial HCl pressure was selected as the range of growth parameters in this study.

2.3.2 Crystallinity and purity of CVT-Grown NiO crystals

The most favorable growth conditions were obtained at 1400K using an initial HCl pressure of 250 torr. At these conditions, the average growth rate was over than 100 μm/hour. Figure 2.9 illustrates examples of the single crystals and bicrystals that were successfully grown. The colorless parts of the specimens are the MgO substrates and green deposits of smaller diameter (which appear to be black in Fig. 2.9) are the CVT-grown NiO crystals. The thickness of the epitaxial layers may be seen to range up to ~1mm.

The grown NiO crystal could be easily detached from the MgO substrate by preferentially dissolving off the MgO substrate in hot (190°C) 85% H₃PO₄
Fig. 2.9 CVT-grown single crystals and bicrystals with $\Sigma 5$ and $\Sigma 13$ tilt grain boundaries. The 2nd and 3rd specimens from the left are single crystals of NiO. The 3rd one has been removed from the MgO substrate to provide a free-standing crystal. The remaining specimens are bicrystals shown prior to the removal of the MgO substrate.
solution. This process provided free-standing NiO crystals. Such specimens could subsequently be heated in diffusion annealings or in other property measurements without the occurrence of inter-diffusion with the substrate or grain-boundary diffusion of impurities from the substrate into the boundary in the fabricated bicrystal. In Fig. 2.9, the 3rd specimen from the left is an example of a free-standing NiO single crystal. The shiny smooth surface was originally interfaced with the MgO substrate, which verifies that removing the MgO substrate is complete without any loss of the grown NiO crystal. Using this free-standing single crystal of NiO, a Laue back-reflection experiment was done to check the single crystallinity. The diffraction pattern is shown in Fig. 2.10. The sharp and symmetric X-ray diffraction spots verify that the CVT-grown NiO crystal was indeed a very high quality single crystal. There is no evidence for subgrains with large mosaic spread.

The NiO single crystals and bicrystals commonly displayed facets (Fig. 2.11 and Fig. 2.12). Figure 2.12(a) shows an NiO bicrystal with a $\Sigma 5$ symmetric tilt boundary in epitaxial orientation on the (001) surface of the MgO substrate. The equal sizes of the symmetrically-related re-entrant planes at one end of the bicrystal show that the grain boundary in the bicrystal remained exactly normal to the (001) surface of the substrate as the deposit grew. These facets are clearly shown at higher magnification in the scanning electron micrograph of Fig. 2.12(b). The high uniform reflectivity across these surfaces also indicates the absence of low-angle grain boundaries and suggests crystals with a high degree of mechanical perfection.

High Resolution Transmission Electron Microscopy (HRTEM) was employed to investigate the atomic-scale structure at a $\Sigma 13$ symmetric tilt boundary (Fig. 2.13). The micrograph indicates that the CVT-grown bicrystal has indeed a grain boundary that is free from second phases or precipitates on an atomic scale.
Fig. 2.10  Laue back-reflection diffraction pattern of NiO single crystal, which says that the grown deposit is single crystal indeed.
Fig. 2.11 The morphology of one of the CVT- grown single crystals which displays well-formed highly-planar, very reflective facets intersecting the <100> growth direction.
Fig. 2.12  (a) Optical micrograph of a CVT-grown NiO bicrystal with a $\Sigma 5$ tilt grain boundary.
(b) Scanning Electron Micrograph of the details of the growth morphology of the CVT- grown bicrystal of (a). Note that the two small facets related by the mirror plane of the symmetric tilt boundary have remained of equal size as the thickness of the epitaxial deposit has increased. This indicates that the grain boundary is precisely normal to the substrate.
Fig. 2.13 HRTEM micrograph of a \( \Sigma 13 \) boundary in a grown bicrystal.
Direct measurement on the micrograph of the orientation of <100> on either side of this boundary provides an angle of 17.16(7)° compared to the angle of $2\tan^{-1}(1/5)=22.62°$ at which we attempted to join (510) surfaces of the seed. The misorientation of five and one-half degrees likely resulted during the sawing and polishing of the nominal (510) surfaces during fabrication of the bicrystal seed. An interesting observation is that the grain boundary is not precisely planar on an atomic scale, but is rather a combination of facets of alternating orientation. Merkle et al.[53,54] observed similar microfacets along NiO grain boundaries.

With the substrate material (MgO) removed, the purity of the free-standing NiO crystal was investigated by ICP (Inductively Coupled Plasma) mass spectrometry and neutron activation analysis. The results are shown in Table 2.1. The purity of CVT-grown crystals was very remarkable. ICP analysis showed no concentration of cation impurity elements above the detection limit of the method, on the order of 10 ppm, depending on the particular element. The neutron activation analysis has higher sensitivity for some impurity elements, but is more selective; it can not be applied to all elements. The results of the two analytical methods are consistent, except for the finding of a significant amount of K in the activation analysis (ca. 160 ppm). This may have resulted from a contaminant. Of particular interest is the low level of Cl incorporation (~3 ppm) as revealed by neutron activation analysis although a certain amount of HCl gas (250 torr) was used to transport NiO, which agrees with the result of Gruber[77] found for MgO crystals grown by a similar process.
Table 2.1 Results for Chemical Analysis of CVT-grown NiO crystals

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP analysis* (ppm)</th>
<th>Neutron activation analysis** (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>&lt; 12.1</td>
<td>&lt; 9.644</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt; 2.43</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt; 12.1</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>&lt; 24.3</td>
<td>162.251</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 2.43</td>
<td>0.2</td>
</tr>
<tr>
<td>Na</td>
<td>&lt; 48.5</td>
<td>4.297</td>
</tr>
<tr>
<td>Ni</td>
<td>Major</td>
<td>Major</td>
</tr>
<tr>
<td>Si</td>
<td>&lt; 12.1</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt; 7.28</td>
<td>&lt; 82.057</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt; 16.4</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>3.013 ppm</td>
</tr>
</tbody>
</table>

* : Inductively Coupled Plasma (ICP) analysis performed by Dr. Zamechek, UOP, Tarrytown Analytical Laboratory, Tarrytown, New York

** : Neutron Activation analysis performed by Dr. Ilhan Olmez, M.I.T., Nuclear Reactor Laboratory, Cambridge, MA

- : Not available for a given test
< : Below the detection limit
2.4 Summary

Single crystals having growth direction of <100> and bicrystals of NiO having the symmetric tilt orientations Σ5 (310) and Σ13 (510) were successfully grown epitaxially on MgO substrates at average growth rates greater than 100 µm/hr at a growth temperature of 1400K. The procedure used a CVT reaction that employed HCl as a carrier agent. The crystals have high mechanical perfection as a consequence of having been grown in a small temperature gradient. Single crystals and bicrystals commonly displayed facets along the growth direction. The grain boundary is oriented perpendicular to the (001) surface of the substrate and the deposit. The epitaxial NiO crystals could be easily removed from the MgO substrates by selectively dissolving away the MgO in a hot 85% H₃PO₄ solution. Sharp and symmetric Laue back reflection spots verified a small mosaic spread of subgrains and high quality crystallinity of the CVT-grown NiO single crystals. Chemical analysis of the free-standing NiO crystals by inductively-coupled plasma mass spectrometry and neutron activation analysis revealed no cation element present at concentrations above their individual detection limits (typically on the order of 10 ppm) and Cl, derived from the HCl carrier gas, which is present at a level of less than 3 ppm. These NiO crystals are unique in several respects: (a) detectability of virtually no impurities in the bulk regions; (b) minimal opportunity for these low levels of impurity to segregate to the boundary during growth, thanks to high growth rate at a temperature (1400K) relatively low compared to the melting temperature (2257K); and (c) the ability to remove the epitaxial crystals from its substrate.
The NiO crystals are thus very suitable for use in investigations of structure-property relationships in bulk regions and grain boundaries of controlled geometry.
Chapter III

Analysis of Diffusion Depth Profile for Accurate Grain Boundary Diffusion Coefficient

3.1 Introduction

After completion of a diffusion annealing with grain boundaries of controlled orientation that have been properly characterized, diffusion depth profiles of oxygen isotope can be determined by Secondary Ion Mass Spectroscopy (SIMS) analysis. However, it is not easy to obtain a value for a grain boundary diffusion coefficient from an experimentally-measured diffusion depth profile. Grain boundary transport involves a two dimensional diffusion problem. There simultaneously exist two different kinds of diffusion coefficients (a grain boundary diffusion coefficient and a bulk diffusion coefficient) in a sample, which makes this problem very inaccessible. Only for very limited cases, which have simple boundary conditions and an initial condition, this complex problem can be solved. One of these cases is the problem of constant surface and initial concentrations in a sample, in which one straight grain boundary is perpendicular to the surface. These requirements can be satisfied by an experiment using a bicrystal of the sort whose growth has been described in Chapter II, provided the requirements about constant surface and initial
concentrations in a sample can be controlled in a diffusion experiment. Unfortunately, even for this special case, an exact analytic solution can not be obtained. Instead, only an integral form of a solution could be obtained by Whipple[21]. This means that there is no analytical way to obtain a grain boundary diffusion coefficient from a measured diffusion depth profile.

Therefore, two different approximate methods have been used to obtain a grain boundary diffusion coefficient from an experimentally-obtained diffusion depth profile. They are Fisher's approximate solution[22] and Le Claire's method[23]. Fisher, prior to Whipple's derivation of an exact solution, devised an approximate solution from the describing diffusion equation based on several severe assumptions, among which is the pragmatic assumption that diffusion along the boundary is sufficiently rapid that lateral diffusion from the boundary into the adjacent grains could be satisfactorily described by assuming that the final gradient along the interface was present at all times. This condition can not be assumed automatically and represents a severe approximation. Le Claire's method is based on the Whipple's exact solution. Le Claire built a useful empirical relationship between the slope of a diffusion depth profile and a grain boundary diffusion coefficient by the numerical integration of the Whipple's solution. Since this method used Whipple's exact solution, occasionally it has been misunderstood as an exact solution of the equation describing grain boundary diffusion. However, it should be stressed out here that the Le Claire's method is just an approximate method of analyzing a diffusion depth profile and it is not an exact solution for the equation that describes grain boundary diffusion.

Since the Fisher's approximate solution is an approximate analytic solution, it is well known that a grain boundary diffusion coefficient can not be accurately decided from a diffusion depth profile by this method[21,23,25,26]. On the
other hand, Le Claire's method has been generally used for analysis of grain boundary diffusion experiments without any reservation, because it came from Whipple's exact solution[9,67,70,71]. However, the accuracy of the grain boundary diffusion coefficient obtained by Le Claire's method has hardly been assessed, even though it is a critical factor deciding whether or not this method is acceptable for the conditions of a specific grain boundary diffusion experiment.

From the above considerations several questions arise: How accurate is Le Claire's method for analyzing a diffusion depth profile to obtain a grain boundary diffusion coefficient? Is there any better way than this method? This is the starting point of the work described in this Chapter. The accuracy of Le Claire's method is extensively investigated within a range of experimental parameters that are established as realistic limits on experiments. From the errors established by these calculations, it is clear that an improved way of analyzing a diffusion depth profile is necessary. A new method is indeed established based upon an analysis of concentration gradients that were numerically evaluated from Whipple's exact solution. A two-parameter approximation is fit to these gradients. Values of these parameters were obtained by regression analysis. The approximate solutions thereby obtained are shown to permit extraction of grain-boundary diffusion coefficients that are accurate to within 1% over the entire range of experimental conditions within which experiments are feasible.

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8 There is a huge amount of grain boundary diffusion data in the literature that were evaluated by Le Claire's method. They have been summarized in the book, "Handbook of Grain and Interphase Boundary Diffusion Data", edited by I. Kaur, W. Gust, and L. Kozma, Ziegler Press, Stuttgart(1989). They call the method "Whipple-Le Claire equation", but it is exactly the same as the method developed in Le Claire's paper[23].
3.2 Background

3.2.1 Equations Describing Grain Boundary Diffusion

If material has only one grain boundary of width $2a$ which is parallel to $y$-$z$ plane and perpendicular to $x$-$z$ plane as in Fig. 3.1, grain boundary diffusion can be described as follows:

In the grain boundary region ($|x| < a$),

$$\frac{\partial C'}{\partial t} = D' \left( \frac{\partial^2 C'}{\partial x^2} + \frac{\partial^2 C'}{\partial y^2} \right) \quad (3.1)$$

and for regions outside grain boundary ($|x| > a$),

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) \quad (3.2)$$

where $D$ is the bulk diffusion coefficient, $D'$ is the grain boundary diffusion coefficient, $C$ is the concentration of diffusant in the bulk region ($|x| > a$), and $C'$ is the concentration of diffusant in the grain boundary region ($|x| < a$).

The corresponding boundary conditions and the initial condition can be written as follows:

the boundary conditions,
Fig. 3.1 Schematic diagram which shows a grain boundary of assumed width 2a, and x and y axes normal to and parallel to the interface respectively - the coordinate system used in Eqn. (3.1) and Eqn. (3.2).
\[ C(\pm a, y, t) = C(\pm a, y, t) \] \hspace{1cm} (3.3)

\[ D \frac{\partial C(\pm a, y, t)}{\partial x} = D \frac{\partial C(\pm a, y, t)}{\partial x} \] \hspace{1cm} (3.4)

\[ C(x, 0, t) = C_S \] \hspace{1cm} (3.5)

\[ C(x, \infty, t) = C_0 \] \hspace{1cm} (3.6)

and the initial condition,

\[ C(x, y, 0) = C_0 \] \hspace{1cm} (3.7)

where \( C_S \) is the surface concentration and \( C_0 \) is the initial concentration. The values of \( C_S \) and \( C_0 \) are constants that depend on a particular diffusion experiment.

To describe the diffusion behavior of a solute in the sample, it is necessary to solve the two-dimensional diffusion equations (Eqns. (3.1) and (3.2)) together with the boundary conditions (Eqns. (3.3)-(3.6)) and the initial condition (Eqn. (3.7)).

Whipple solved these complex diffusion equations using Laplace-Fourier transformation [21]. His result was

\[
\frac{C(x, y, t) - C_0}{C_S - C_0} = \text{erfc} \left( \frac{y}{2\sqrt{Dt}} \right) \\
+ \frac{\eta}{2\sqrt{\pi}} \int_1^\infty \frac{\partial \sigma}{\partial \tau} \exp \left( -\frac{\eta^2}{4\sigma} \right) \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \left( \xi + \frac{\sigma - 1}{\beta} \right) \right]
\] \hspace{1cm} (3.8)
where \( \text{erfc} \) is the complementary Gaussian error function, and \( \sigma \) is a variable of integration. The dimensionless variables, \( \Delta = \frac{D'}{D} \) and \( \beta = (\Delta - 1) \frac{a}{\sqrt{Dt}} \) are measures of the magnitude of grain boundary diffusivity relative to that in bulk. The variables, \( \eta = \frac{y}{\sqrt{Dt}} \) and \( \xi = \frac{x-a}{\sqrt{Dt}} \), represent dimensionless coordinates perpendicular to and parallel to the boundary, respectively.

Unfortunately, Eqn. (3.8) is not an analytic solution but an integral form of a solution. The integration step in Eqn. (3.8) makes it very difficult to directly obtain a grain boundary diffusion coefficient, \( D' \), from a measured diffusion depth profile. Whipple used a reasonable assumption to obtain his solution, i.e. a grain boundary width is very small compared to other dimensional quantities. As this is normally true for grain boundary diffusion, this solution may be assumed as the exact solution for the grain boundary diffusion experiment which can be described by Eqns (3.1)-(3.7).

From the SIMS in-depth profiling method or the more traditional mechanical sectioning methods, it is only possible to obtain a concentration averaged along the \( x \) axis, \( C_{\text{avg}}(y,t) \), instead of \( C(x,y,t) \). In other words,

\[
C_{\text{avg}}(y,t) = \frac{\int C(x,y,t) \, dx}{\int dx} = \frac{\int_0^L C(x,y,t) \, dx}{\int_0^L dx}
\]  

(3.9)

where the second integral applies specifically to sputtering with the aid of SIMS over a rectangular area. The edges of the rectangle are assumed to be parallel to, and perpendicular to the exposed boundary, respectively, and \( L \) is the half scanning range of SIMS sputtering in the latter direction.
Applying Eqn. (3.8) to Eqn. (3.9), and using \( a \ll L \), one obtains normalized average concentration, \( \bar{C} \), as

\[
\bar{C} = \frac{C_{\text{avg}}(y,t) - C_0}{C_s - C_0} = \text{erfc}\left(\frac{y}{2\sqrt{Dt}}\right) + \frac{y}{L\sqrt{\pi}} \left[ \int_1^\infty \frac{\partial \sigma}{\sigma^{1.5}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \sqrt{\frac{\Delta-\sigma}{\Delta-1}} \right] \\
\times \left[ \text{ierfc}\left(\frac{1}{2\sqrt{\Delta-\sigma}}\right) \right] - \text{ierfc}\left(\frac{1}{2\sqrt{\Delta-\sigma}} \left(\frac{L-a}{\sqrt{Dt}} + \frac{\sigma-1}{\beta}\right)\right) 
\]

(3.10)

It can easily be recognized that the first part of Eqn. (3.10) comes solely from bulk diffusion. Consequently the second part of Eqn. (3.10) represents the additional solute that is contributed by rapid diffusion along the grain boundary. A typical behavior of Eqn. (3.10) is shown in Fig. 3.2. The contribution of bulk diffusion, the first part of Eqn. (3.10), vanishes quickly with increasing depth, but the contribution of grain boundary diffusion, the second part of Eqn. (3.10), persists above background concentration to much greater depths along the \( y \) axis. Occasionally this contribution of grain boundary diffusion after the bulk diffusion has vanished is referred to as a "tail", which reflects its shape. A detailed derivation of Eqns. (3.8) and (3.10) are described for reference in Appendix A.

3.2.2 Le Claire's Method[23]

Le Claire's method was developed from the definition of parameters in Eqn. (3.8);
Fig. 3.2 A typical diffusion depth profile in a grain-boundary diffusion experiment showing that the contribution from a grain boundary remains as a "tail" while the contribution from bulk diffusion decays very quickly at deeper depths.
Using Eqn. (3.12) simple algebra gives,

\[ \beta = (\Delta - 1) \frac{a}{\sqrt{Dt}} \]  
(3.11),

\[ \eta = \frac{y}{\sqrt{Dt}} \]  
(3.12),

\[ \Delta = \frac{D}{D_t} \]  
(3.13).

Using Eqn. (3.12) simple algebra gives,

\[
\beta = \left( \frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \right)^{5/3} = \left( \frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \right)^{5/3} \frac{1}{\frac{1}{D_t}} \]
\[ = \left( \frac{\partial \ln \bar{C}}{\partial y^{6/5}} \right)^{5/3} \frac{1}{D_t} \]  
(3.14).

Since \( \Delta \gg 1 \) is expected for the transport properties of most grain boundaries, a useful relationship can be derived from Eqn. (3.14) with Eqns. (3.11) and (3.13).

\[ D' a = \left( \frac{D}{t} \right)^{0.5} \left( -\frac{\partial \ln \bar{C}}{\partial (\eta / \sqrt{\beta})^{6/5}} \right)^{5/3} \left( -\frac{\partial \ln \bar{C}}{\partial y^{6/5}} \right)^{-5/3} \]  
(3.15)

Using numerical evaluation of Whipple's solution to examine the dependence of average solute concentration on some function of penetration, Le Claire found that \( \frac{\partial \ln \bar{C}}{\partial (\eta / \sqrt{\beta})^{6/5}} \) approaches -0.78 if \( \beta \) is greater than 10 and \( \eta / \sqrt{\beta} \) is greater than 2.(Fig. 3.3) In doing, Le Claire also claimed that Fisher's equation is not an accurate means for obtaining a grain boundary diffusion coefficient from a
Fig. 3.3 The change of slopes of $\log C \sim \eta/\sqrt{\beta}$ and $\log C \sim (\eta/\sqrt{\beta})^{6/5}$ as a function of $\beta$[23]. There are four kinds of lines in this figure: a short dashed line, an unbroken line, a dotted line named as "Fisher", and a long dashed line. The long dashed line should be read with the scale for $-\frac{\partial \ln C}{\partial \left(\eta/\sqrt{\beta}\right)^{6/5}}$ which appears at the lower right portion of the figure. The remainder of the plots should be read with the scale of $-\frac{\partial \ln C}{\partial \left(\eta/\sqrt{\beta}\right)}$. The unbroken line is the result of numerical calculation and the short dashed line comes from Whipple's asymptotic solution[21]. The dotted line so labeled corresponds to the results obtained by Fisher's method[22].
diffusion depth profile. Substituting \( \frac{\partial \ln \bar{C}}{\partial (\eta / \sqrt{\beta})^{6/5}} \) value as -0.78 into Eqn. (3.15) gives,

\[
D' a = \left( \frac{D}{t} \right)^{0.5} (0.78)^{5/3} \left( -\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \right)^{-5/3} \quad (3.16)
\]

From Eqn. (3.16), the product of grain boundary half-width and grain boundary diffusivity, \( aD' \), can be obtained easily from the slope of a diffusion depth profile. This equation has been widely used to obtain grain boundary diffusion coefficients in most recent grain boundary diffusion studies as mentioned in the introductory part of this chapter.

### 3.2.3 The Factors of Grain Boundary Diffusion Experiments

An interesting aspect of Eqn. (3.16) is that this equation is not a derived solution based on the equations of grain boundary diffusion. The result is based upon the definition of parameters and simple algebra combined with the key discovery of Le Claire - the empirical result that the value of \( \frac{\partial \ln \bar{C}}{\partial (\eta / \sqrt{\beta})^{6/5}} \) in Eqn. (3.15) approaches -0.78 when \( \beta \) is greater than 10 and \( \eta / \sqrt{\beta} \) is greater than 2. Le Claire's method is somewhat unclear as a guide to the design of experiments with conditions under which the result is applicable. From Eqn. (3.12) it is obvious that \( \eta \) is a function of the bulk diffusion coefficient, \( D \), which means
that the value of $\eta$ can be easily controlled once $D$ is determined from a bulk diffusion experiment prior to the grain boundary diffusion experiment. However, $\beta$ is a function of both the bulk diffusion coefficient, $D$, and the grain boundary diffusion coefficient, $D'$, which can be clearly seen in the definitions of Eqn. (3.11) and Eqn. (3.13). Before $D'$ is determined, $\beta$ remains as an undefined variable. This means that it is impossible to select a useful range of $\eta / \sqrt{\beta}$ within which Eqn. (3.16) is valid in advance of the experiment that produces the diffusion depth profile. In planning experiments, a method which depends only on the range of $\eta$ would be much more practical than a method which depends on $\eta / \sqrt{\beta}$. Then following questions should then be resolved: 1) What range of $\eta$ should be counted in a grain boundary diffusion experiment? 2) How accurate is Le Claire's method in that range of $\eta$? 3) Is it possible to devise an improved method that gives grain boundary diffusivity of higher accuracy for that $\eta$ range?

Regions that correspond to large $\eta$ values should be avoided since large $\eta$ would require that low concentrations of diffusant be detected in the sample. This causes difficulty in measuring the concentration of diffusant accurately. The situation becomes critical in the experiment where a background concentration of diffusant initially exists in the diffusion sample, for example $^{18}$O in-diffusion experiment into oxides. There is a natural abundance of $^{18}$O concentration of 0.2039% in the sample before an in-diffusion experiment. If the concentration of diffusant differs only by a few ppm from the background concentration level, it is completely impossible to obtain a diffusion depth profile accurately from that sample. That diffusion depth profile will just be buried in the background concentration. The same argument can be extended to $^{18}$O out-diffusion experiments from sample intentionally enriched in $^{18}$O.
We also need a region for which there is no contribution from bulk diffusion (See Fig. 3.2) to make the analysis as simple as Le Claire's method and Fisher's method.

From the above considerations, it is reasonable to fix the $\eta$ range as $6 \sim 10$, which is equivalent to $6\sqrt{Dt} \leq y \leq 10\sqrt{Dt}$, in the sense that this range gives a detectable amount of diffusant concentration and there is no significant contribution of bulk diffusion.
3.3 Calculation Procedure

From Eqn. (3.14), an alternative form of Le Claire's method can be written as,

\[
\beta = \left( \frac{-0.78}{\frac{\partial \ln C}{\partial \eta^{6/5}}} \right)^{5/3}
\]  

(3.17).

This equation has every aspect of Le Claire's equation, Eqn. (3.16), in the sense that \( \beta \) is directly related to \( aD \) by Eqn. (3.11) and (3.13). The error in \( aD \) which is obtained by Le Claire's method, Eqn. (3.16), should thus be the same as the error in \( \beta \) of Eqn. (3.17).

Checking the accuracy of Le Claire's method could be done by the following steps; (1) Calculating \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) as a function of \( \eta \) for specific input values of \( \beta = \beta_{in} \), (2) Calculating \( \beta = \beta_{out} \) using Eqn. (3.17), (3) Comparing input \( \beta \) value, \( \beta_{in} \), with output \( \beta \) value, \( \beta_{out} \).

Using second part of Eqn. (3.10), which is the part solely coming from grain boundary diffusion without bulk diffusion,

\[
\frac{\partial \ln C}{\partial \eta^{6/5}} = \frac{I_1 - \frac{\eta^2}{2} I_2}{1.2 \eta^{1.2} I_1}
\]  

(3.18)

where
\[
I_1 = \int_1^\infty \frac{\partial \sigma}{\sigma^{1/5}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \sqrt{\frac{\Delta - \sigma}{\Delta - 1}} \\
\times \left\{ \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1 - \sigma}{\Delta - \sigma}} \right] - \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \left( \frac{L-a}{\sqrt{Dt}} + \frac{\sigma-1}{\beta} \right) \right] \right\}
\]

(3.19)

and

\[
I_2 = \int_1^\infty \frac{\partial \sigma}{\sigma^{2.5}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \sqrt{\frac{\Delta - \sigma}{\Delta - 1}} \\
\times \left\{ \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1 - \sigma}{\Delta - \sigma}} \right] - \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \left( \frac{L-a}{\sqrt{Dt}} + \frac{\sigma-1}{\beta} \right) \right] \right\}
\]

(3.20)

As may be seen in the above equations, \( \Delta \) and \( L \) also appear as variables in addition to \( \beta \) and \( \eta \) in the integrals \( I_1 \) and \( I_2 \). Firstly it would be desirable to remove the variables, \( \Delta \) and \( L \), to simplify the calculations. As described in Appendix C, \( I_1 \) and \( I_2 \) can be approximated as follows to within a 1% error in \( \frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \) if \( \frac{\Delta}{\beta} \left( = \frac{\sqrt{Dt}}{a} \right) \) is greater than 10³ and \( L \) is greater than 4\( \sqrt{Dt} \):

\[
I_1 = \left[ \int_1^\infty \frac{\partial \sigma}{\sigma^{1.5}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \text{erfc} \left[ \frac{1}{2} \frac{\sigma-1}{\beta} \right] \right]
\]

(3.21)

and

\[
I_2 = \left[ \int_1^\infty \frac{\partial \sigma}{\sigma^{2.5}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \text{erfc} \left[ \frac{1}{2} \frac{\sigma-1}{\beta} \right] \right]
\]

(3.22)
The two assumptions, that \( \frac{\Delta}{\beta} \left( = \frac{\sqrt{D} t}{a} \right) \) be greater than \( 10^3 \) and \( L \) be greater than \( 4 \sqrt{D} t \), can be easily achieved by controlling time, \( t \), of the diffusion annealing experiment.

Using Eqn. (3.18), (3.21), and (3.22), \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) is calculated numerically* as a function of \( \beta_{in} \) and \( \eta \). In Appendix B the various aspects of this numerical integration are described. From this \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) value, \( \beta_{out} \) is obtained using Eqn. (3.17). The ratio \( \beta_{out} \) to \( \beta_{in} \) provides a measure of the accuracy of Le Claire's method in obtaining a grain boundary diffusion coefficient from a diffusion depth profile. In other words,

\[
\frac{\beta_{out}}{\beta_{in}} = \frac{D_{out}}{D_{in}} = \frac{D_{Le Claire}}{D_{real}}
\]

(3.23)

where \( D_{real} \) is the true input grain boundary diffusion coefficient used to compute the gradient and \( D_{Le Claire} \) is the output grain boundary diffusion coefficient from Eqn. (3.17).

* Mathematica program, v. 2.2 1., Student version, L2332-8826, Wolfram Research, 1993
3.4 Results and Discussion

3.4.1 The Assessment of Le Claire's Method

The result of computations of $\frac{D_{\text{Le Claire}}}{D_{\text{real}}}$ as a function of $\eta$ for various values of $\beta$ are shown in Fig. 3.4. It may be readily noticed that Le Claire's method is acceptable only when $\beta$ is around 10. The error becomes progressively larger as $\beta$ increases within this range of $\eta$. The variation of relative error between the real value and the one obtained from Le Claire's method, which can be expressed as $\frac{D_{\text{Le Claire}}}{D_{\text{real}}}$, is summarized in Table 3.1. Surprisingly, Le Claire's method produces inaccurate grain boundary diffusion coefficients having errors as large as 74% relative to the real grain boundary diffusion coefficients in this $\eta$ range.

The values of $\frac{\partial \ln \overline{C}}{\partial (\eta \sqrt{\beta})^{6/5}}$ are shown in Fig. 3.5. If Le Claire's method is correct in this $\eta$ range, these values should converge to -0.78. However, the value of $\frac{\partial \ln \overline{C}}{\partial (\eta \sqrt{\beta})^{6/5}}$ clearly deviates widely from -0.78.

To check whether the calculations are correct, $\frac{\partial \ln \overline{C}}{\partial (\eta \sqrt{\beta})^{6/5}}$ is calculated as a function of $\frac{\eta}{\sqrt{\beta}}$ (as done by Le Claire) in Fig. 3.6. The calculated result coincides with Le Claire's result (Fig. 3.3)-not perfectly but approximately in the range of $\eta$ for which Le Claire did calculate values of $\frac{\partial \ln \overline{C}}{\partial (\eta \sqrt{\beta})^{6/5}}$ ($\frac{\eta}{\sqrt{\beta}}$ is greater than 2). The discrepancies amount to ±5%. This confirms that the inaccuracy
Fig. 3.4 The ratio of grain boundary diffusivity obtained from Le Claire’s method to the input grain boundary diffusivity. It is seen that Le Claire’s method is not accurate in this range of $6 \leq \eta \leq 10$. 
Table 3.1 The accuracy of Le Claire's method for various values of $\beta$

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>( \frac{D'<em>{\text{Le Claire}}}{D</em>{\text{real}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.15 $\sim$ 1.24</td>
</tr>
<tr>
<td>10</td>
<td>0.97 $\sim$ 1.03</td>
</tr>
<tr>
<td>100</td>
<td>0.74 $\sim$ 0.84</td>
</tr>
<tr>
<td>1000</td>
<td>0.53 $\sim$ 0.61</td>
</tr>
<tr>
<td>10000</td>
<td>0.37 $\sim$ 0.42</td>
</tr>
<tr>
<td>100000</td>
<td>0.26 $\sim$ 0.30</td>
</tr>
</tbody>
</table>
Fig. 3.5 The value of $\frac{\partial \ln C}{\partial (\eta/\sqrt{\beta})^{6/5}}$ in the range of $6 \leq \eta \leq 10$ a slope which is supposed to be -0.78 if Le Claire’s method is correct.
Fig. 3.6(a) The variation of $\frac{\partial \ln \bar{C}}{\partial (\eta/\sqrt{\beta})^{6/5}}$ in the range of $\eta/\sqrt{\beta} \leq 20$. (For $\beta \geq 100$ the lines overlap with each other and cannot be distinguished.)
Fig. 3.6(b) The variation of $\frac{D'_{\text{Le Claire}}}{D_{\text{real}}}$ in the range of $\frac{\eta}{\sqrt{\beta}} \leq 20$. (For $\beta \geq 100$ the lines overlap and cannot be distinguished.)
produced by Le Claire's method does not come from incorrect calculation, if we allow ±5% errors as reasonable. Le Claire simply did not include the meaningful range of grain boundary diffusion experiments, $6\sqrt{Dt} \leq y \leq 10\sqrt{Dt}$.

3.4.2 An Improved Relation for Obtaining Grain Boundary Diffusion Coefficients from Experimental Concentration Gradients

In light of the results of the preceding section how, then, might we obtain accurate grain boundary diffusion coefficients from diffusion depth profiles in the range of $6\sqrt{Dt} \leq y \leq 10\sqrt{Dt}$, which has been established as a meaningful range of oxygen self-diffusion distances in oxide systems? To achieve this purpose, the ranges of values of $\beta$ were divided into 5 different subsets of ranges. Values of $\beta$ were examined at equally-spaced intervals within each group of $\beta$ as follows;

(i) $1 \leq \beta \leq 10$, \hspace{1cm} $\beta = 1, 2, 3, \cdots, 9, 10 \times 10^0$

(ii) $10 \leq \beta \leq 10^2$, \hspace{1cm} $\beta = 1, 2, 3, \cdots, 9, 10 \times 10^1$

(iii) $10^2 \leq \beta \leq 10^3$, \hspace{1cm} $\beta = 1, 2, 3, \cdots, 9, 10 \times 10^2$

(iv) $10^3 \leq \beta \leq 10^4$, \hspace{1cm} $\beta = 1, 2, 3, \cdots, 9, 10 \times 10^3$

(v) $10^4 \leq \beta \leq 10^5$, \hspace{1cm} $\beta = 1, 2, 3, \cdots, 9, 10 \times 10^4$

For each $\beta$, the value of $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ was computed as a function of $\eta$ ($6 \leq \eta \leq 10$). The average value of $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ for each $\beta$ was then obtained from the values
Table 3.2 The values of constants, A and B, computed for an improved expression of the form

\[ \beta = 10^A \left( - \frac{\partial \ln \bar{C}}{\partial \eta^{1.2}} \right)^B \]

for various ranges of \( \beta \)

<table>
<thead>
<tr>
<th>( \beta )</th>
<th>( \frac{\partial \ln \bar{C}}{\partial \eta^{1.2}} )</th>
<th>A</th>
<th>B</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ~ 10</td>
<td>-0.702627 ~ -0.195588</td>
<td>-0.274313</td>
<td>-1.797654</td>
<td>0.99999</td>
</tr>
<tr>
<td>10 ~ 100</td>
<td>-0.195588 ~ -0.056815</td>
<td>-0.326028</td>
<td>-1.865051</td>
<td>0.99997</td>
</tr>
<tr>
<td>100 ~ 1000</td>
<td>-0.056815 ~ -0.0173545</td>
<td>-0.422809</td>
<td>-1.943238</td>
<td>0.99999</td>
</tr>
<tr>
<td>1000 ~ 10000</td>
<td>-0.0173545 ~ -0.005417876</td>
<td>-0.484307</td>
<td>-1.978574</td>
<td>0.99999</td>
</tr>
<tr>
<td>10000 ~ 100000</td>
<td>-0.005417876 ~ -0.001694886</td>
<td>-0.498762</td>
<td>-1.985363</td>
<td>0.99999</td>
</tr>
</tbody>
</table>
obtained over the range $6 \leq \eta \leq 10$. This step of averaging $\frac{\partial \ln C}{\partial \eta^{6/5}}$ is physically meaningful since the averaged value of $\frac{\partial \ln C}{\partial \eta^{6/5}}$ is the resultant quantity involved in a fit of a measured diffusion depth profile to a single slope over its entire experimental range. Using these pairs of values for $\frac{\partial \ln C}{\partial \eta^{6/5}}$ and $\beta$, a log-log regression analysis of the form,

$$\beta = 10^A \left( \frac{-\partial \ln C}{\partial \eta^{6/5}} \right)^B$$

(3.24)

where $A$ and $B$ are adjustable parameters, was performed within each range of $\beta$. The result of the computations is shown in Table 3.2. As shown, the result of the regression analysis is marvelously precise! The $R$ factor which indicates the success of the fitting is unity within, at worst, three parts in $10^5$. Back substitution of the value of $\frac{\partial \ln C}{\partial \eta^{6/5}}$ to the equation of Table 3.2 yields a value of $\beta$ which has error within 1% with respect to the actual value of $\beta$ that was used in computing the gradient. (Table 3.3 and Fig. 3.7)

As shown previously in Table 3.1, Le Claire's method to obtain grain boundary diffusion coefficients in the range of $6 \leq \eta \leq 10$ produces errors as large as 74% when $\beta$ equals $10^5$. More seriously the error increases strongly with increasing $\beta$. Instead, present regression results give very accurate grain boundary diffusion coefficients, with 1% error at most, for all feasible range of grain boundary diffusion experiments ($1 \leq \beta \leq 10^5$) and not just $\beta = 10$. 

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Table 3.3 Comparison between the value of $\beta_{in}$ used as input for numerical evaluation and the value of $\beta_{est.}$ estimated by regression analysis

<table>
<thead>
<tr>
<th>Beta</th>
<th>Beta est.</th>
<th>%Dev</th>
<th>Beta</th>
<th>Beta est.</th>
<th>%Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0028</td>
<td>0.282</td>
<td>600</td>
<td>600.72</td>
<td>0.120</td>
</tr>
<tr>
<td>2</td>
<td>1.9926</td>
<td>0.368</td>
<td>700</td>
<td>699.99</td>
<td>0.001</td>
</tr>
<tr>
<td>3</td>
<td>2.9947</td>
<td>0.177</td>
<td>800</td>
<td>799.01</td>
<td>0.124</td>
</tr>
<tr>
<td>4</td>
<td>3.9996</td>
<td>0.009</td>
<td>900</td>
<td>897.81</td>
<td>0.244</td>
</tr>
<tr>
<td>5</td>
<td>5.0042</td>
<td>0.085</td>
<td>1000</td>
<td>996.40</td>
<td>0.360</td>
</tr>
<tr>
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<td>6.0071</td>
<td>0.118</td>
<td>2000</td>
<td>2001.8</td>
<td>0.089</td>
</tr>
<tr>
<td>7</td>
<td>7.0074</td>
<td>0.106</td>
<td>3000</td>
<td>3003.8</td>
<td>0.128</td>
</tr>
<tr>
<td>8</td>
<td>8.0049</td>
<td>0.061</td>
<td>4000</td>
<td>4004.5</td>
<td>0.112</td>
</tr>
<tr>
<td>9</td>
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<td>0.006</td>
<td>5000</td>
<td>5003.9</td>
<td>0.078</td>
</tr>
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</tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>70</td>
<td>70.011</td>
<td>0.016</td>
<td>30000</td>
<td>29996.0</td>
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<tr>
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<td>40000</td>
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<tr>
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</tr>
<tr>
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<tr>
<td>500</td>
<td>501.18</td>
<td>0.235</td>
<td>100000</td>
<td>100554.0</td>
<td>0.554</td>
</tr>
</tbody>
</table>
The comparison between $\beta_{in}$ and $\beta$ coming from the regression result, Table 3.2. The results show a perfect match with each other.
The procedure for obtaining an accurate grain boundary diffusion coefficient from a diffusion depth profile by means of the present method can be summarized as follows:

1) From a bulk diffusion experiment, find a bulk diffusion coefficient, \( D \).

2) Experimentally determine the average diffusion depth profile in the range of
\[
\frac{\sqrt{Dt}}{a} \geq 10^3 \quad \text{and} \quad L \geq 4\sqrt{Dt}.
\]

3) Calculate the mean slope \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) in the range of
\[
6\sqrt{Dt} \leq y \leq 10\sqrt{Dt}
\]
from a plot of \( \ln C \) as a function of \( \eta^{6/5} \).

4) Substitute the value of \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) into Eqn. 3.24, using the appropriate parameters of Table 3.2 after finding the proper range of \( \beta \) to which the measured \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) corresponds.

5) Convert the obtained \( \beta \) to a grain boundary diffusion coefficient, \( aD' \), using Eqn. (3.11) and Eqn. (3.13).

Since this method uses the slope of a diffusion depth profile instead of the absolute quantity of the concentration, it can be used for any sectioning experiment and not just for SIMS depth profiling data.

To check the validity, this method was applied to an existing diffusion data\[78\], Fig. 3.8. Here, the bulk diffusivity, \( D \), was reported as \( 2.62 \times 10^{-16} \text{cm}^2/\text{sec} \) and the annealing time was 7hr. In the original work, the range selected for analysis was 100nm ~ 500nm, which corresponds to \( 3.89\sqrt{Dt} ~ 19.46\sqrt{Dt} \). On the other hand, to apply the new method, we only need the range \( 6\sqrt{Dt} ~ 10\sqrt{Dt} \), which corresponds to 154nm ~ 257nm, Fig. 3.9. The value calculated for \( \beta \) was 201.42 from that region. The result is summarized in Table 3.4. We can regard the grain boundary diffusivity which was obtained by the newly-developed method as a true value since it has been shown to have error within 1% when analyzing a
Fig. 3.8 The concentration gradient for reanalysis[78]. The data was obtained from a MgO bicrystal which has a $\Sigma 13$ grain boundary annealed at 1400$^\circ$C for 7hr. The region used in the original work[78] for analysis of diffusion depth profile, 100nm~500nm, is highlighted.
Fig. 3.9 The concentration gradient which was adapted from Fig. 3.7 for reanalysis. The region (154nm~257nm) which was used for reanalysis is highlighted.
Table 3.4 The comparison of grain boundary diffusivity, $D'$, from reanalysis of an existing diffusion data[78]

<table>
<thead>
<tr>
<th>Method</th>
<th>Diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>New method</td>
<td>$(2.71 \pm 0.24) \times 10^{-12} \text{cm}^2 / \text{sec}$</td>
</tr>
<tr>
<td>Le Claire's method</td>
<td>$(1.03 \pm 0.02) \times 10^{-12} \text{cm}^2 / \text{sec}$</td>
</tr>
<tr>
<td>Fisher's method</td>
<td>$(4.92 \pm 0.12) \times 10^{-13} \text{cm}^2 / \text{sec}$</td>
</tr>
</tbody>
</table>
diffusion depth profile. As can be seen, the grain boundary diffusivity obtained by Le Claire's analysis clearly underestimated the true grain boundary diffusivity, and the relative error amounts to 62%. As a matter of fact, the range used for analysis, 100nm ~ 500nm, corresponds to \( 0.274 \leq \frac{\eta}{\sqrt{\beta}} \leq 1.371 \). This range is clearly outside the region for which Le Claire's method is valid \( \frac{\eta}{\sqrt{\beta}} \geq 2 \). This explains why Le Claire's method produced a very inaccurate value for the grain boundary diffusivity. To satisfy the condition \( \frac{\eta}{\sqrt{\beta}} \geq 2 \), we need a region, \( \geq 729 \text{nm} \), in the present case. However, we lack data corresponding to that region in the data for diffusion depth profile. This is another advantage in using our new method instead of Le Claire's method in analyzing diffusion depth profiles to obtain grain boundary diffusivity.
3.5 Summary

Le Claire's equation for obtaining a grain boundary diffusion coefficient, \( D' \), was shown not to be an accurate method in the range of solute penetrations \( 6\sqrt{Dt} \leq y \leq 10\sqrt{Dt} \) which is the meaningful range of depth profiling experiments, especially for oxygen self-diffusion in oxide systems. For this range, the value of \( D' \) obtained from Le Claire's method introduces an error as large as 74% and at least of a few percent in the range of \( 1 \leq \beta \leq 10^5 \). This discrepancy comes from the fact that in this \( y \) range the value of \( \frac{\partial \ln C}{\partial (\eta/\sqrt{\beta})^{6/5}} \) is not close to -0.78, the empirical observation on which the method is based. By numerical computation it has been confirmed that the value of \( \frac{\partial \ln C}{\partial (\eta/\sqrt{\beta})^{6/5}} \) converges to -0.78 only if \( \frac{\eta}{\sqrt{\beta}} \geq 2 \). By log-log regression of \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) and \( \beta \), a method which can give accurate grain boundary diffusion coefficients to within 1% error at most for all ranges of \( \beta \) has been proposed, using a relation of the form

\[
\beta = 10^A \left( \frac{\partial \ln C}{\partial \eta^{6/5}} \right)^B.
\]

In this expression A and B are constants, whose value depends on the range of \( \beta \), determined by fits to gradients that were numerically calculated from Whipple's exact integral solution to the diffusion equations.
Chapter IV

Enhanced Diffusion due to Potential Gradients around Grain Boundaries

4.1 Introduction

In ionic systems, owing to the difference in the formation energy of pairs of intrinsic defects at free surfaces or grain boundaries, there is a defect concentration gradient (or equivalently speaking, a potential gradient) in the bulk region close to such interfaces[1]. The variation of the cation and anion defect -concentrations near a grain boundary in NaCl is shown schematically in Fig. 4.1. This defect concentration gradient has importance on diffusion since a diffusion coefficient is directly proportional to a defect concentration in an ionic system. It is generally appreciated that enhanced diffusion along a grain boundary may partly arise because of such defect concentration gradients close to the boundary[3]. There are two major contributions to the enhanced diffusion along grain boundaries in an oxide system. The first is from the grain boundary structure itself, and the second from the built-up defect concentration close to grain boundaries and on the grain boundary core. It is interesting that in recent observations of grain boundaries in ionic crystals performed with High Resolution TEM(HRTEM), normal crystal structure is maintained right up to a grain boundary and there is not a well-
Fig. 4.1  Schematic diagram of the variation of defect concentrations for intrinsic defects close to a surface or grain boundary in pure NaCl[1]. The difference arises from differences in the formation energy of each defect.
defined grain-boundary region[53,78]. The thickness of the grain boundary is normally assumed as ~1nm on a rather arbitrary basis.

It is impossible to experimentally know the contribution of the space charge region to grain boundary diffusion without the presence of the different structure at the grain boundary core. In contrast, this can be done relatively easily using calculation. In other words, we can model the situation by neglecting the thickness of grain boundary, which agrees with the usual HRTEM observation and assume that there is only a defect concentration gradient, as illustrated in Fig. 4.2. Thirdly, one can then solve the proper diffusion equation with boundary and initial conditions, and obtain a concentration profile of diffusant in the sample. From this concentration profile, we can see the effect of a potential gradient on the enhanced diffusion along a grain boundary. From this computational procedure the effect of a potential gradient can be interpreted in the terms of a usual grain boundary diffusion experiment. That is, converting a continuously-varying bulk diffusion coefficient adjacent to a boundary to an equivalent product of a constant grain boundary diffusion coefficient times a grain boundary width, the product in terms of which the grain boundary diffusion problem is usually formulated.

In analyzing a concentration gradient of diffusant to obtain an effective grain boundary diffusion product, \( aD' \), special attention should be given to the means of analysis because it is not a simple task to obtain a grain boundary diffusion coefficient from a concentration profile as has been stated in Chapter III. Actually, there is no analytical expression from which one can obtain a grain boundary diffusion coefficient from a concentration profile. Only approximations have been used to obtain grain boundary diffusion
Fig. 4.2  Schematic representation of the possible variation in concentration of the major defect around a grain boundary. The thickness of the grain boundary is neglected.
coefficients[22,23]. It is certainly not possible to obtain an accurate grain boundary diffusion coefficient and to separate the effect of a potential gradient from the influence of boundary structure. Fortunately, in Chapter III a method for obtaining accurate grain-boundary diffusion products, $aD$, (within 1% error) from concentration profiles was devised. In this Chapter, the method is used to calculate effective grain boundary diffusion coefficients from virtual diffusion-annealing experiments. This will provide a measure of the value of an effective product $aD$ that would result from application of the standard high-diffusivity slab model to solute gradients actually produced by space-charge distributions.

One problem is encountered in attempting to solve a 2-dimensional diffusion equation with a varying diffusion coefficient. It is almost impossible to solve this equation analytically. Consequently, the Finite Difference Method (FDM) of numerical analysis is instead applied to obtain numerical solutions to the partial differential equations[108,109]. In applying the FDM, careful attention is given to insure that the solution is not affected by the choice of grid size or the time-step size, as can easily be the case.

The system will be restricted to intrinsic cases in this study meaning that no effects of doping by other species will be considered. For extrinsic cases it is not possible to solve a Poisson equation analytically to relate a defect concentration gradient and a potential gradient.

Basically, from the results of this chapter the effect of a space charge region on enhanced diffusion can be easily calculated in terms of the standard grain boundary diffusion product $aD$ once the potential at the bulk region and the relative dielectric constant of the system are known.
4.2 Background

When intrinsic disorder is introduced near an interface in a perfect crystal, the total free energy of the system is changed. After minimization of free energy of the system, the defect concentration in the system can be expressed as follows[1];

\[
\frac{n_i(x)}{N} = \exp \left[ -\frac{\left(g_{n_i} + z_i e \phi(x)\right)}{kT} \right]
\]  \hspace{1cm} (4.1)

where \(N\) is the density of lattice sites in the crystal, \(n_i(x)\) is the density of the charged defect \(i\) at \(x\), \(g_{n_i}\) is the formation energy of defect \(i\), \(z_i\) is the effective charge of defect \(i\), \(\phi(x)\) is the potential at \(x\), and \(x\) is the measured distance from the grain boundary.

At \(x = \infty\), in the bulk region, Eqn. (4.1) becomes,

\[
\frac{n_{i\infty}}{N} = \exp \left[ -\frac{\left(g_{n_i} + z_i e \phi_\infty\right)}{kT} \right]
\]  \hspace{1cm} (4.2)

where \(n_{i\infty}\) is the density of charged defect \(i\) and \(\phi_\infty\) is the potential in the bulk region far from a grain boundary, respectively.

From Eqn. (4.1) and (4.2)

\[
\frac{n_i(x)}{n_{i\infty}} = \exp \left[ -z_i e (\phi(x) - \phi_\infty) \right]
\]  \hspace{1cm} (4.3)
The diffusion coefficient of species $I$, $D_I$, corresponding to defect $i$ (for example, $I$ can be a oxygen ion and defect $i$ can be a oxygen vacancy or oxygen interstitial) is directly proportional to defect concentration of $i$, which means

$$D_I \propto n_i \quad (4.4).$$

From Eqn. (4.3) and (4.4)

$$D_I(x) = D_{I\infty} \times \exp\left[\frac{-z_i e (\phi(x) - \phi_\infty)}{kT}\right] \quad (4.5)$$

where $D_{I\infty}$ is the bulk diffusion coefficient of species $I$.

For intrinsic cases (no doping by other species), $\frac{z_i e (\phi(x) - \phi_\infty)}{kT}$ of Eqn. (4.5) can be expressed as follows[1]:

$$\frac{z_i e (\phi(x) - \phi_\infty)}{kT} = 4 \tanh^{-1}\left[\exp\left(-\frac{x}{\delta}\right) \tanh\left(-\frac{z_i e \phi_\infty}{4kT}\right)\right] \quad (4.6)$$

$$\delta^{-2} = \frac{2z_i^2 e^2 N}{\varepsilon_0 \varepsilon_r kT} \exp\left(-\frac{g_{n_i} + z_i e \phi_\infty}{kT}\right) \quad (4.7)$$

where $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon_r$ is the static relative dielectric constant. The quantity $\delta$ is called Debye length. Here Eqn. (4.6) results from solving a Poisson equation.
The diffusion equation that governs the usual grain boundary diffusion experiment can be described relative to the coordinate system defined in Fig. 4.3 with proper boundary and initial conditions as follows:

\[
\frac{\partial C_I(x,y,t)}{\partial t} = \nabla \cdot [D_I(x) \nabla C_I(x,y,t)]
\]  

(4.8)

The boundary conditions are

\[ C_I(x,0,t) = 1 \]  

(4.9),

\[ C_I(x,\infty,t) = 0 \]  

(4.10),

and

\[ \left( \frac{\partial C_I}{\partial x} \right)_{x=\pm\infty} = 0 \]  

(4.11).

An initial condition is

\[ C_I(x,y,0) = 0 \]  

(4.12).

where \( C_I \) is the concentration of species \( I \). As shown in Fig. 4.3 and the above equations a semi-infinite medium with constant surface and initial conditions is assumed.

Substitution of Eqn. (4.5) in Eqn. (4.8) gives

\[
\frac{\partial C_I}{\partial t} = (D_{Io} \times A(x)) \left( \frac{\partial C_I}{\partial x} \right) + (D_{Io} \times B(x)) \left[ \frac{\partial^2 C_I}{\partial x^2} + \frac{\partial^2 C_I}{\partial y^2} \right]
\]  

(4.13)

where
Fig. 4.3 Schematic illustration of a bicrystal sample in a diffusion experiment showing the orientation of the x axis and y axis in Eqn. (4.8).
\[ B(x) = \exp\left[ -4 \tanh^{-1}\left( \exp\left( -\frac{x}{\delta} \right) \tanh\left( -\frac{z_i e \phi_\infty}{4kT} \right) \right) \right] \quad (4.14) \]

and

\[ A(x) = \frac{4 \delta^{-1} \exp\left( -\frac{x}{\delta} \right) \tanh\left( -\frac{z_i e \phi_\infty}{4kT} \right)}{1 - \left[ \exp\left( -\frac{x}{\delta} \right) \tanh\left( -\frac{z_i e \phi_\infty}{4kT} \right) \right]^2} \times B(x) \quad (4.15). \]

We need to solve this rather complex 2-dimensional diffusion equation with a positionally-varying diffusion coefficient and the proper boundary and initial conditions, Eqns. (4.9)-(4.12). Here it is interesting to note that \( \frac{z_i e \phi_\infty}{kT} \) always appears as a combined quantity in the above equations. This means that \( \frac{z_i e \phi_\infty}{kT} \) can be regarded as a single variable in the calculation. Also, it is worth indicating that in the diffusion equation, Eqn. (4.13), an extra term that involves \( \frac{\partial C}{\partial x} \) (the first term of the right side of the equation) since \( D_1(x) \) is a function of \( x \).
4.3 Calculation Procedure

The Finite Difference Method (FDM) is applied to solve Eqn. (4.13), since it cannot be solved analytically.

To simplify Eqn. (4.13), the following parameters are defined:

\[
X = \frac{x}{\delta} \quad (4.16)
\]

\[
Y = \frac{y}{\delta} \quad (4.17)
\]

\[
T = \frac{D_{f} \times t}{\delta^2} \quad (4.18)
\]

Equation (4.13) can then be expressed in the compact form:

\[
\frac{\partial C_L}{\partial T} = A(X) \left( \frac{\partial C_L}{\partial X} \right) + B(X) \left[ \frac{\partial^2 C_L}{\partial X^2} + \frac{\partial^2 C_L}{\partial Y^2} \right] \quad (4.19)
\]

where

\[
B(X) = \exp \left[ -4 \tanh^{-1} \left( \exp(-X) \tanh \left( -\frac{z_i e \phi_{\infty}}{4kT} \right) \right) \right] \quad (4.20)
\]

\[
A(X) = \frac{4 \exp(-X) \tanh \left( -\frac{z_i e \phi_{\infty}}{4kT} \right)}{1 - \left[ \exp(-X) \tanh \left( -\frac{z_i e \phi_{\infty}}{4kT} \right) \right]^2} \times B(X) \quad (4.21)
\]
In this study, the Crank-Nicolson method was used among the several FDMs which can be applied to the diffusion equation, since the Crank-Nicolson method is always stable no matter what time step is used and is accurate in the sense that local truncation error is order $2^{109}$. Stability of the numerical method is very important in this case because of the variation of the diffusion coefficient along the $x$ direction. The extent of the change of diffusion coefficient increases exponentially as $\frac{z\phi_\infty}{kT}$ changes. (Fig. 4.4(b))

Applying the FDM to Eqn. (4.19) using Crank-Nicolson method,

$$
\frac{C_{i,j,k+1} - C_{i,j,k}}{\Delta t} = A(i) \left( \frac{C_{i+1,j,k+1} - C_{i-1,j,k+1}}{4\Delta x} + \frac{C_{i+1,j,k} - C_{i-1,j,k}}{4\Delta x} \right)
+ B(i) \left( \frac{C_{i+1,j,k+1} - 2C_{i,j,k+1} + C_{i-1,j,k+1}}{2\Delta x^2} + \frac{C_{i+1,j,k} - 2C_{i,j,k} + C_{i-1,j,k}}{2\Delta x^2} \right)
+ \frac{C_{i,j+1,k+1} - 2C_{i,j,k+1} + C_{i,j-1,k+1}}{2\Delta y^2} + \frac{C_{i,j+1,k} - 2C_{i,j,k} + C_{i,j-1,k}}{2\Delta y^2}
$$

where $\Delta x$, $\Delta y$, and $\Delta t$ are the spatial and temporal increments.

Re-arranging Eqn. (4.22),

$$
a_1(i)C_{i-1,j,k+1} + b_1(i)C_{i,j-1,k+1} + c_1(i)C_{i,j,k+1} + d_1(i)C_{i,j+1,k+1} + e_1(i)C_{i+1,j,k+1} = a_2(i)C_{i-1,j,k} + b_2(i)C_{i,j-1,k} + c_2(i)C_{i,j,k} + d_2(i)C_{i,j+1,k} + e_2(i)C_{i+1,j,k}
$$

where

$$
a_1(i) = A(i) \frac{\Delta t}{4\Delta x} - B(i) \frac{\Delta t}{2\Delta x^2}
$$

$$
b_1(i) = -B(i) \frac{\Delta t}{2\Delta x^2}
$$

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\[ c_1(i) = 1 + B(i) \frac{1}{h^2} + B(i) \frac{1}{k^2} \quad (4.26) \]
\[ d_1(i) = -B(i) \frac{1}{2k^2} \quad (4.27) \]
\[ e_1(i) = -A(i) \frac{1}{4h} - B(i) \frac{1}{2h^2} \quad (4.28) \]
\[ a_2(i) = -A(i) \frac{1}{4h} + B(i) \frac{1}{2h^2} \quad (4.29) \]
\[ b_2(i) = B(i) \frac{1}{2k^2} \quad (4.30) \]
\[ c_2(i) = 1 - B(i) \frac{1}{h^2} - B(i) \frac{1}{k^2} \quad (4.31) \]
\[ d_2(i) = B(i) \frac{1}{2k^2} \quad (4.32) \]
\[ e_2(i) = A(i) \frac{1}{4h} + B(i) \frac{1}{2h^2} \quad (4.33). \]

Since \( C(x,y,t) \) should be equal to \( C(-x,y,t) \), only the region of \( x \geq 0 \) needs to be considered. (Fig. 4.2) When applying the FDM, finite boundary values are required, but we only have boundary conditions at infinity, Eqns. (4.10)-(4.11). Therefore, it is required to introduce the boundary values at reasonable finite limits. The regions used to calculate \( C(x,y,t) \) are as follows:

\[ 0 \leq X \leq 6 \quad (\Rightarrow 0 \leq x \leq 6\sqrt{D_{\infty}t}) \quad (4.34) \]
\[ 0 \leq Y \leq 15 \quad (\Rightarrow 0 \leq y \leq 15\sqrt{D_{\infty}t}) \quad (4.35) \]
\[ 0 \leq T \leq 1 \quad \left( \Rightarrow 0 \leq t \leq \frac{D_{\infty}t}{\delta^2} \right) \quad (4.36) \]

where \( \delta = \sqrt{D_{\infty}t} \).

The setting of \( \delta = \sqrt{D_{\infty}t} \) is rather arbitrary because \( D_{\infty}t \) can be controlled freely by selection of a diffusion annealing time, \( t \). The \( X \) range and \( Y \) range is set
to include all possible contributions of the potential gradient around a grain boundary.

From the initial condition and boundary conditions, $C(x,y,t)$ can be computed from Eqn. (4.13) by matrix operation. If the number of grid points along the $x$ axis is $n_x$ and the number of grid points along the $y$ axis is $n_y$, the matrix to be handled during the calculation of Eqn. (4.23) becomes $n_x \times n_y$ by $n_x \times n_y$ matrix, since we need to put a 2 dimensional format into a 1 dimensional format. If $n_x$ and $n_y$ equals 30 respectively, the matrix to be handled becomes 900 by 900, which is a typical size for such studies. A fast computer is required to handle Eqn. (4.23).* The MATLAB codes for this calculation are listed in Appendix F.

In performing the FDM, $C_f(X,Y,T)$ is calculated for different values of $\frac{z_i e \Phi_\infty}{kT}$ in the range of 1.5~5 after considering a realistic experimental range for these parameters. Once a concentration profile is obtained, the average concentration along $x$ axis, $\overline{C_f}(Y,T)$ can be easily calculated using the trapezoidal method as follows;

\[
\overline{C_f}(Y,T) = \frac{\int_0^6 C_f(X,Y,T)dX}{\int_0^6 dX} = \frac{\sum_{i=0}^{n_x-1} (C_i(X,Y,T) + C_{i+1}(X,Y,T)) \times \Delta x_i}{12} \quad (4.37)
\]

One can then calculate the value of $-\frac{\partial \ln \overline{C_f}}{\partial y^{6/5}}$ using $\overline{C_f}(Y,T)$ between $6 \leq Y \leq 10$ ($\Leftrightarrow 6\sqrt{D_{\infty t}} \leq y \leq 10\sqrt{D_{\infty t}}$). From this slope, an effective value of $\beta$ may be established through use of the new method of Chapter III, Table 4.1.

By definition[21],

* MATLAB v.4.1.1 with a IBM RISC/6000 workstation
where $D_{gb}$ is the grain boundary diffusion coefficient and $a$ is the half width of the grain boundary.

For the specific computations of this analysis, the value of the time of the diffusion annealing, $t$, was selected to provide the special relation,

$$\sqrt{D_{gb} t} = \delta$$

Then, from Eqn. (4.38), this special relation provides

$$\frac{D_{gb}}{D_{\infty}} = 1 + \beta \frac{\delta}{a}$$

The above consideration indicates that once $\beta$ is calculated from $\bar{C}_t(Y,T)$ for various values of $\frac{z_i e \phi_{\infty}}{kT}$, the enhanced diffusion can be easily expressed in terms of an effective grain boundary diffusion coefficient. In other words, once $\frac{z_i e \phi_{\infty}}{kT}$ and $\delta$ are established, we can see the effect of the enhancement of bulk diffusion due to a potential gradient adjacent to a grain boundary in terms of the equivalent slab of constant diffusivity that would produce essentially the same solute gradient.
4.4 Results and Discussion

When the FDM is applied, stability and accuracy have to be considered. Since the Crank-Nicolson method is used, there is no worry about the stability but accuracy still need to be considered. In other words, the influence of grid size should be excluded. One way to do this is to change grid size and step size, and find the region within which the result of the calculation does not change within a desired level of accuracy.

Special attention should be given to the shape of the $D_l(x)/D_{l_{\infty}}$. As shown in Fig. 4.4, as $z_i e \phi_{\infty}/kT$ is varied, the shape of $D_l(x)/D_{l_{\infty}}$ changes in addition to the change in the absolute value of $D_l(x)/D_{l_{\infty}}$. Most of the variation in $D_l(x)/D_{l_{\infty}}$ occurs in the region of $x < 1 \sqrt{D_{l_{\infty}}} = 1\delta$. This means that when we perform the FDM calculation, special attention has to be given to this region compared to other regions. Otherwise, we could not count the whole characteristic of $D_l(x)/D_{l_{\infty}}$ when the FDM is applied to this diffusion study.

For this purpose two different size of grid were used along the $x$ axis: $h1$ (for $0 \leq x \leq 1$) and $h2$ (for $1 \leq x \leq 6$). The details of the corresponding Crank-Nicolson method for the two different grid sizes is discussed in Appendix D.

In Fig. 4.5 the effect of the choice of $h1$ is investigated for $z_i e \phi_{\infty}/kT = 5$ while $h2$ equal to 0.5, $k$ equal to 0.5, and $l$ equal to 0.001. As $h1$ becomes smaller, $\beta$ increases and becomes saturated when $h2$ equals 0.05. This observation shows that when we use a rather large value of $h1$, we simply cannot count the full shape of $D_l(x)/D_{l_{\infty}}$ and simply miss some part. From this observation, $h1$ is selected as 0.05 for this study. This is a safe assumption.
Fig. 4.4(a) The variation of $D(x)/D(0)$ as a function of $x/\delta$ for various values of $z_{\text{eff}}\phi_{\infty}/kT$. The results show that most of the variation in $D(x)/D(0)$ occurs in the region of $x \leq 1\delta$. 
Fig. 4.4(b) The variation of $D(0)/D_\infty$ as a function of $z_i e \phi_\infty / kT$, which shows an exponential change of $D(0)/D_\infty$. 
Fig. 4.5 Effect of the value of $h_1$ on $\beta$ determination in the FDM method when $\frac{z_i e \phi_\infty}{kT} = 5$, $h_2=0.5$, $k=0.5$, and $l=0.001$. The results verify that use of a value of $h_1$ as 0.05 is safe in this study.
since in the range of interest (1.5~5) the shape of $D_l(x)/D_{lo}$ is not as sharp as that of $\frac{z_i e \Phi_{\infty}}{kT}$ equals 5, which means that, if we set $h_1$ equal to 0.05, all aspects of $D_l(x)/D_{lo}$ in the FDM will be counted.

Also the effect of step size, $\Delta t$, is investigated by changing the number of steps, $n_t$, Fig. 4.6. If $n_t$ is greater than 100, no significant difference in $\beta$ could be noticed. In this study $n_t = 1000$ is selected.

Using the conditions that $h_1$ equals 0.05, $h_2$ equals 0.5, $k$ equals 0.5, and $l$ equals 0.001, $C(x,y,t)$ was calculated, Fig. 4.7, for $\frac{z_i e \Phi_{\infty}}{kT} = 5$. Due to the effect of the grain boundary potential, there is an extra concentration as $x$ approaches 0, which is close to grain boundary. The effect of the grain boundary potential can be more clearly seen if $\bar{C}(y,t)$ is calculated using Eqn. (4.37). In Fig. 4.8, $\bar{C}(y,t)$ is compared with the concentration coming from bulk diffusion alone, which is given by $\text{erfc}(y/(4Dt)^{1/2})$. In Fig. 4.9 $\bar{C}(y,t)$ is also compared with the concentration coming from the potential effect alone—that is, $\bar{C}(y,t)$ with bulk diffusion subtracted. Figure 4.8 and Fig. 4.9 both show a dependence of average concentration on solute penetration which is typical of that seen in grain boundary diffusion experiments[72].

Figure 4.10 shows the value of $-\frac{\partial \ln \bar{C}_l}{\partial y^{6/5}}$ as a function of $\frac{z_i e \Phi_{\infty}}{kT}$, and Fig. 4.11 shows the corresponding values of $\beta$ evaluated from the gradient by means of the parameters listed in Table 4.1. As shown, $\beta$ grows exponentially as $\frac{z_i e \Phi_{\infty}}{kT}$ increases, which means that as $\frac{z_i e \Phi_{\infty}}{kT}$ value varies from 1.5 to 5, $\beta$ varies from 0.67 to 8.54. Using these data, a polynomial regression of order 3 has been performed. The regression incorporated the fact that $\beta$ should go to zero at $\frac{z_i e \Phi_{\infty}}{kT} = 0$, based on the fact that if there is no potential, $\frac{D_{gb}}{D_{lo}}$ should be equal to 1 in Eqn. (4.38). The result of regression is as follows;
\[ \beta = (0.564 \pm 0.030)a + (-0.194 \pm 0.017)a^2 + (0.0845 \pm 0.0024)a^3 \]  

(4.41)

where \( a = \frac{ze\phi_\infty}{kT} \). The R factor for this regression is 0.999977, which shows a good degree of fitting, and that the relative error of \( \beta \) obtained from Eqn. (4.41) is within 1% compared with the actual computed values of \( \beta \) that were used in the fit.

This is a very interesting result since if a value of \( \frac{ze\phi_\infty}{kT} \) is known, a value of \( \beta \) can be easily calculated from Eqn. (4.41). Furthermore, if the dielectric constant is known, the value of \( \beta \) can be easily converted using Eqn. (4.40) to \( \frac{D_gb}{D_\infty} \) which is a quantity that expresses the enhancement of diffusivity along the grain boundary relative to bulk diffusivity.

There is one more thing to be mentioned in this study. In Eqn. (4.4) \( \frac{z_ie(\phi(x) - \phi_\infty)}{kT} \) can be approximated as follows[6];

\[ \frac{z_ie(\phi(x) - \phi_\infty)}{kT} = - \frac{z_ie\phi_\infty}{kT} \exp\left(-\frac{x}{\delta}\right) \]  

(4.42)

This approximation is much simpler than the exact solution, Eqn. (4.6). However, validity of this approximation can be checked. In Fig. 4.12, \( \frac{D(x)}{D_\infty} \) coming from Eqn. (4.6) and Eqn. (4.42) are compared at \( \frac{z_ie\phi_\infty}{kT} \) equals 5. As may be seen, the exact solution decays much faster than the approximation.

In Fig. 4.13, the values of \( \beta \) that may be calculated using this approximation in the FDM are plotted as a function of \( \frac{z_ie\phi_\infty}{kT} \) and compared with the values of \( \beta \) from that are obtained with the exact solution. In the range of small
Fig. 4.6 Effect of time step size ($l = T/nt$) on the determination of $\beta$ in the FDM method when \( \frac{z_i e^{\phi_{\infty}}}{kT} = 5 \), $h_1=0.05$, $h_2=0.5$, and $k=0.5$. The results show that use of a value of $l$ as 0.001 is safe in this study.
Fig. 4.7  Concentration profile obtained by solving the 2-dimensional diffusion equation, Eqn. (4.8), with the FDM method when \( \frac{z\epsilon \phi_\infty}{kT} = 5 \), \( h_1 = 0.05 \), \( h_2 = 0.5 \), \( k = 0.5 \), \( l = 0.01 \).
Fig. 4.8  Comparison of $\bar{C}(y,t)$ obtained from Eqn. (4.37) with the value obtained from a bulk diffusion experiment.
Fig. 4.9  Comparison of $\bar{C}(y,t)$ obtained from Eqn. (4.37), with the contribution to the concentration profile that arises only from the grain-boundary potential effect, that is $\bar{C}(y,t)$ minus the contribution of bulk diffusion.
Fig. 4.10 The value of \( \frac{\partial \ln \bar{C}_I}{\partial \eta_0} \) obtained from the concentration profiles as a function of \( \frac{z_i e \phi_\infty}{kT} \).

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Fig. 4.11 The values of $\beta$ obtained from $\frac{\partial \ln \bar{C}}{\partial y^{6/5}}$ using the improved method of Chapter III, Table 3.2, as a function of $\frac{z_i e \phi_\infty}{kT}$. 
Table 4.1 The constants, A and B, for $\beta = 10^A \left(\frac{-\partial \ln \tilde{C}}{\partial Y^{1.2}}\right)^B$ for various regions of $\frac{-\partial \ln \tilde{C}}{\partial Y^{1.2}}$ from Chapter III

<table>
<thead>
<tr>
<th>$\frac{-\partial \ln \tilde{C}}{\partial Y^{1.2}}$</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.702627 $\sim$ -0.195588</td>
<td>-0.274313</td>
<td>-1.797654</td>
</tr>
<tr>
<td>-0.195588 $\sim$ -0.056815</td>
<td>-0.326028</td>
<td>-1.865051</td>
</tr>
<tr>
<td>-0.056815 $\sim$ -0.0173545</td>
<td>-0.422809</td>
<td>-1.943238</td>
</tr>
<tr>
<td>-0.0173545 $\sim$ -0.005417876</td>
<td>-0.484307</td>
<td>-1.978574</td>
</tr>
<tr>
<td>-0.005417876 $\sim$ -0.001694886</td>
<td>-0.498762</td>
<td>-1.985363</td>
</tr>
</tbody>
</table>
Fig. 4.12 Comparison of $D(x)/D_\infty$ coming from the exact expression for the potential distribution, Eqn. (4.6), and the approximation, Eqn. (4.42), when $\frac{z_i e \phi_\infty}{kT}$ equals 5. Note that the ratio of Eqn. (4.6) decays much faster than that of Eqn. (4.42).
Fig. 4.13 Comparison of values of $\beta$ coming from the exact expression for the potential distribution, Eqn. (4.6), and the approximation, Eqn. (4.42), as a function of $z_i e \phi_\infty / kT$. The discrepancy between the two expressions increases as $z_i e \phi_\infty / kT$ becomes larger.
\( \frac{z_i e \phi_{\infty}}{kT} \), the two methods results in almost same value of \( \beta \). However, as \( \frac{z_i e \phi_{\infty}}{kT} \) becomes large, there is an increasing discrepancy between the results of the two methods. Therefore Eqn. (4.42) should not be used at large value of \( \frac{z_i e \phi_{\infty}}{kT} \).

For further reference, the results of calculations of \( C(x,y,t) \) are assembled for various values of \( \frac{z_i e \phi_{\infty}}{kT} \) with Eqn. (4.6) or Eqn. (4.42) in Appendix E.

It is interesting to apply the result of this Chapter to Ti grain boundary diffusion in the TiO\(_2\) system. The used data are as follows[6]:

- **System**: Pure TiO\(_2\) (stoichiometric system)
- **Intrinsic disorder**: Frenkel disorder (\( Ti_i \) or \( V_{Ti} \))
- **Temperature**: 1350°C
  - \( g_{Ti_i} \): 2 eV
  - \( g_{V_{Ti}} \): 2.5 eV
  - \( \delta \): 93.4 Å
  - \( z \): 4

Then

\[
e \phi_{\infty} = \frac{1}{8} \left( g_{V_{Ti}} - g_{Ti_i} \right) = 0.0625eV
\]

\[
\frac{z e \phi_{\infty}}{kT} = 1.7844
\]

\[
\frac{\delta}{a} = \frac{93.4}{5} = 18.68.
\]

Using Eqn. (4.41) \( \beta \) is calculated as 0.8688, and from Eqn. (4.40) \( \frac{D_{gb}}{D_{bulk}} \) can be calculated as 17.23, which is the enhancement of diffusivity compared to bulk
diffusivity. It should be stressed here that this enhancement is the quantity expressed as a grain boundary diffusivity not the whole bulk diffusivity. This calculation indicates that the contribution of the space charge region to grain boundary diffusivity is very small for the case of Ti diffusion in stoichiometric TiO$_2$. Similarly, the core charge distribution and effects of the different structure at the boundary core are likely to make more significant contributions to any enhancement in spite of the fact that there is no evidence for a distinct grain boundary region of appreciable width according to HRTEM study[7].
4.5 Summary

The effect of space charge region on enhanced diffusion was quantitatively studied by solving a 2-dimensional diffusion equation with a diffusion coefficient whose magnitude varied with distance from the grain boundary. To solve the diffusion equation, the FDM was applied since it is hard to solve such 2-dimensional diffusion equations analytically. In application of the FDM, effect of grid size and time step size was carefully investigated to correctly include the shape of $\frac{D(x)}{D_\infty}$ to the FDM. After solving the diffusion equation to obtain a concentration profile, an effective value of $\beta$ was calculated by the method of Chapter III. It was confirmed that a space charge region can not explain the magnitude of the enhanced diffusion along grain boundaries that has been observed in many systems.
Chapter V

Various Aspects of Application of the Finite Difference Method to Bulk Diffusion Studies

5.1 Introduction

Predicting the diffusion behavior in a medium with a diffusion equation having boundary conditions and initial conditions requires solving partial differential equations. This costs a great deal of mathematical time and may be practically impossible if the initial conditions and the boundary conditions are complex. Only for special cases for which the boundary and initial conditions are very simple, is it feasible to obtain an analytic solution to the diffusion equation. However, actual diffusion experiments involve rather complex conditions. Simple analytic solutions devised for application to diffusion experiments, are likely to be only approximate solutions, valid for a limited range of experimental conditions and of limited accuracy. For example, in a diffusion experiment an infinite medium and a constant surface concentration may be assumed. But, practically, it is impossible to fabricate an infinite medium and keep even less possible to a constant surface concentration during a diffusion experiment, which may last for a very long period of time. Compared to analytic solution, numerical analysis can
provide a solution to the diffusion equation under any circumstances for which boundary and initial conditions can be defined.

In many diffusion experiments the diffusion coefficient can be assumed to be a constant. The diffusion equation (also known as the heat equation) then has the form of Eqn. (5.1):

\[
\frac{\partial C}{\partial t} = D \nabla^2 C
\]  

(5.1)

where \( C \) is the concentration of diffusing species and \( D \) is the diffusion coefficient.

There are many ways of applying the Finite Difference Method to the diffusion equation, Eqn. (5.1), including the Forward-Difference method, the Backward-Difference method, and the Crank-Nicolson method\[108,109\].

When the Finite Difference Method is applied to solve the diffusion equation, two main factors should be considered, namely stability and accuracy. It is well known that the Forward-Difference method has a limited range of stability but the Backward-Difference method and the Crank-Nicolson method are always stable. In the matter of accuracy, the Forward-Difference and the Backward-Difference methods are order 1 and the Crank-Nicolson method is order 2, which means that the Crank-Nicolson method is more accurate than the other two methods\[108,109\].

Among the above methods, the Forward-Difference method is the most efficient in the sense of computing time. The Forward-Difference method does not require computing an inverse matrix, a crucial and time-consuming part of the Backward-Difference method and the Crank-Nicolson method. Also, inversion of a matrix makes the resulting matrix less sparse (that is, more elements are non-zero), and this means that more computing time is
required for subsequent matrix operations. Nevertheless, the Forward-Difference method has not been applied frequently to solve the diffusion equation because it has a drawback in stability. It is known that the value of \( \lambda (= \frac{D \Delta t}{\Delta x^2} \), as defined in the following section) should be less than 0.5 for the Forward-Difference method to be stable[108,109]. This limits the range of application of that method. In this study, a constant diffusion coefficient was assumed. This means that the value of \( \lambda \) could be easily controlled within a region of stability. However, the accuracy of this method for a certain value of \( \lambda \) is not known although it is a critical factor in deciding whether or not the Forward-Difference method may be used to solve the diffusion equation within a desired accuracy. If the Forward-Difference method can predict the solution to the diffusion equation in an acceptable range of accuracy for a certain value of \( \lambda \), the sluggish Crank-Nicolson method does not have to be applied in order to insure stability of the solution.

To examine these questions in this study the Forward-Difference and the Crank-Nicolson methods have both been carefully applied to a rather simple 1-dimensional diffusion equation for which an exact analytic solution is available. The problem is bulk diffusion in a specimen maintained at constant surface concentration, an experiment that has been frequently used to obtain diffusion data. The solution is the well-known complementary error function distribution of solute. When applying the two methods to this diffusion equation, various \( \lambda \) values smaller than 0.5 were used. The degree of deviation degree of the numerical solution from the known analytic solution was monitored to check the accuracy of these two methods.
5.2 Computational procedure

The situation examined in this study was as follows;

(i) The 1-dimensional diffusion equation,

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{5.2} \]

for \( x \geq 0, \ t \geq 0 \)

(ii) The boundary conditions

\[ C(0,t) = 1 \tag{5.3} \]

and

\[ C(\infty, t) = 0 \tag{5.4} \]

(iii) The initial condition

\[ C(x,0) = 0 \tag{5.5} \]

The analytic solution to this problem is well known, namely;

\[ C(x,t) = \text{Erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \tag{5.6} \]

There are two problems when the Finite Difference Method is applied to this specific case. The first thing is having specified a boundary condition where \( x \) equals infinity. However, in the Finite Difference Method a finite boundary is always required. The boundary at \( x = \infty \) was approximated in this study as being at \( x = 6.4\sqrt{Dt} \). The actual concentration at this position is
$6.0257 \times 10^{-6}$ (\(\Leftarrow C(6.4\sqrt{Dt},t) = Erfc(3.2)\)) which could be taken as zero for present purposes. The second problem is the inconsistency of the limiting values of the initial condition and the boundary condition at \(C(0,0)\), that is;

\[
\lim_{t \to 0} C(0,t) = 1 \quad (5.7)
\]

but

\[
\lim_{x \to 0} C(x,0) = 0 \quad (5.8)
\]

This problem could be handled by averaging the two limits[110], Eqn. (5.7) and Eqn. (5.8), in other words

\[
C(0,0) = \frac{1}{2}(1 + 0) = 0.5
\]

The effect of averaging the two limits is discussed in Appendix G by comparing the results evaluated for the case of \(C(0,0)=0\) and the case of \(C(0,0)=1\).

Except for the above two considerations, the usual procedures of the Finite Difference Method were used. If \(\Delta x\) is a grid size and \(\Delta t\) is a time step, for the Forward-Difference method[109],

\[
C_{i,j+1} = \lambda C_{i+1,j} + (1 - 2\lambda)C_{i,j} + \lambda C_{i-1,j} \quad (5.9)
\]

and for the Crank-Nicolson method[109],

\[
-\frac{\lambda}{2} \lambda C_{i+1,j+1} + (1 + \lambda)C_{i,j+1} - \frac{\lambda}{2} C_{i-1,j+1}
\]

\[
= \frac{\lambda}{2} \lambda C_{i+1,j} + (1 - \lambda)C_{i,j} + \frac{\lambda}{2} C_{i-1,j} \quad (5.10)
\]
where
\[ \lambda = \frac{D \Delta t}{\Delta x^2} \]  
\[ (5.11). \]

In this study, the \( x \) axis was divided into 100 steps, which means \( \Delta x \) was 0.064\( \sqrt{D \Delta t} \), and \( \Delta t \) was specified by the value desired for \( \lambda \).

The emulation of Eqn. (5.9) and (5.10) were performed by MATLAB\(^*\). By varying \( \Delta t \), the effect of \( \lambda \) was investigated. The range of \( \lambda \) was selected as 0.001~0.4 after considering conditions that would permit evaluation with reasonable range of computing time within the stability region of the Forward-Difference method, as mentioned earlier. After obtaining \( C(x,t) \) by both numerical methods, the Forward-Difference method and the Crank-Nicolson method, the accuracy was monitored by calculating the error, \( e \), in the result by calculating the difference between the analytic solution and the numerical result as follows;

\[ e = C(x,t) - C_n(x,t) \]  
\[ (5.12) \]

where \( C(x,t) \) is the analytic solution and \( C_n(x,t) \) is the numerical solution.

\* MATLAB v.4.1.1 with a IBM RISC/6000 workstation
5.3 Results and Discussion

In Fig. 5.1 and Fig. 5.2, the error, \( e \), has been evaluated for the Forward-Difference method and for the Crank-Nicolson method, respectively. An interesting result evident in Fig. 5.1 is that the absolute value of the error for the Forward-Difference method decreases as \( \lambda \) decreases in the range of \( (\lambda > -0.2) \) but it then once again increases for further decrease in \( \lambda \) within a small \( \lambda \) region \( (\lambda < -0.1) \). On the other hand, the Crank-Nicolson method, unlike the Forward-Difference method, has no such tendency.

For the Forward-Difference method, the maximum error, \( e_{\text{max}} \), which occurred at \( \sim 2.76\sqrt{Dt} \) in Fig. 5.1, is plotted as a function of \( \lambda \) in Fig. 5.3. Surprisingly, the result shows a remarkably good linear relationship between \( e_{\text{max}} \) and \( \lambda \). The result of a linear regression of the data is as follows,

\[
e_{\text{max}} = -5.55998 \times 10^{-5} + 3.33628 \times 10^{-4} \lambda
\]

\( R = 0.99999998 \)

where \( R \), the correlation coefficient, indicates the degree of fitting to this linear regression equation. In Eqn. (5.13) evidently \( e_{\text{max}} \) becomes zero at \( \lambda \) value of \( \sim 0.1667 \). If \( e_{\text{max}} \) becomes zero, in Fig. 5.1 the error should be zero for the entire range of \( x \) at this value of \( \lambda \). This means that the results of the Forward-Difference method contain no error at all for all regions of \( x \) if the \( \lambda \) value is set to 0.1667. To confirm this prediction, a \( \lambda \) value of 0.1667 was applied to Eqn. (5.9). The result is shown in Fig. 5.4 along with the previous
Fig. 5.1 The variation of error between an analytic solution and the Forward-Difference method as a function of $x$ with various $\lambda$ values.
Fig. 5.2 The variation of error between an analytic solution and the Crank-Nicolson method as a function of $x$ with various $\lambda$ values.
Fig. 5.3  Result of a least-squares fitting between the maximum error and the value of $\lambda$ employed in the Forward-Difference method.
Fig. 5.4  A plot showing that at $\lambda$ equals 1/6 there is no significant error for the entire $x$ range when the Forward-Difference method is applied.
results of Fig. 5.1. As can be seen, there is indeed no significant error for any value of $x$ when this $\lambda$ value is employed. This is a strange feature of the Finite Difference Method. Since the Finite Difference Method uses a finite grid size, $\Delta x$, and a time step, $\Delta t$, the numerical solution cannot be accurate as the analytic solution. Error would be expected in this method. According to Fig. 5.3, however, no error results from application of the Forward-Difference method at $\lambda$ value of 0.1667. Mathematical analysis can explain that the Forward-Difference method becomes very accurate at this specific $\lambda$ (=1/6) value, coming from the fact that the accuracy changes to order 2 from order 1 through cancellation of the respective errors associated with the $x$ axis and $t$ axis[11,12]. On the other hand, the Crank-Nicolson method (Fig. 5.2) does not display the same tendency as the Forward-Difference method. There might be no advantage of using the Crank-Nicolson method in this $\lambda$ range from the standpoint of accuracy. However, the Crank-Nicolson method can be a powerful tool in cases where the diffusion coefficient is not constant since in that case controlling the value of $\lambda$ in a stability region is very difficult. Although mathematical analysis can explain the observation that the accuracy jumps to order 2 for the Forward-Difference method when $\lambda$ equals 1/6, it is still interesting to interpret this $\lambda$ value in a physical sense. For the 1-dimensional diffusion equation, the corresponding continuity equation is

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

(5.14).

The change in the amount of concentration of the diffusing species during $\Delta t$ is
\[ \int_{t_0}^{t_0 + \Delta t} \frac{\partial C}{\partial t} \, dt = -\int_{t_0}^{t_0 + \Delta t} \frac{\partial J}{\partial x} \, dt \]  \hspace{1cm} (5.15) \]

If \( \Delta t \) and \( \Delta x \) are small enough to be assumed as \( dt \) and \( dx \), Eqn. (5.15) can be written as

\[ \Delta C(t_0 \rightarrow t_0 + \Delta t) = -\frac{\Delta J}{\Delta x}(t_0 \rightarrow t_0 + \Delta t) \]  \hspace{1cm} (5.16) \]

When this situation is applied to the Finite-Difference Method scheme, Fig. 5.5, \( \Delta C \) and \( \Delta J \) are

\[ \Delta C = C_{i,j+1} - C_{i,j} \]  \hspace{1cm} (5.17) \]

and

\[ \Delta J = J_{\text{in}} - J_{\text{out}} \]  \hspace{1cm} (5.18) \]

It can be easily recognized that \( J_{\text{in}} \) and \( J_{\text{out}} \) have the following form:\[113],

\[ J_{\text{in}} = \frac{1}{6} \left( C_{i,j} - C_{i-1,j} \right) \frac{h}{k} \]  \hspace{1cm} (5.19) \]

and

\[ J_{\text{out}} = \frac{1}{6} \left( C_{i+1,j} - C_{i,j} \right) \frac{h}{k} \]  \hspace{1cm} (5.20) \]

Using Eqn. (5.17)-(5.20), \( \Delta x = h \), and \( \Delta t = k \), Eqn. (5.16) becomes,

\[ C_{i,j+1} = \frac{1}{6} C_{i-1,j} + \frac{4}{6} C_{i,j} + \frac{1}{6} C_{i+1,j} \]  \hspace{1cm} (5.21) \]
Fig. 5.5 Schematic illustration of the finite difference scheme in the x and t axes.
which is exactly same as the equation of the Forward-Difference method, Eqn. (5.9), when \( \lambda \) equals \( 1/6 \).

From the above verification, it is shown that the Forward-Difference method exactly simulates the atomistic diffusion of migrating species. Consequently, the Forward-Difference method becomes very accurate at this value of \( \lambda \).

These interesting observations related to the Forward-Difference method could be regarded as a strange coincidence coming from two weak points of this bulk diffusion analysis, (1) the discontinuity of the two limits, Eqn. (5.7) and Eqn. (5.8), (2) changing an infinite boundary value to a finite boundary value, \( 6.4\sqrt{Dt} \) or \( 8\sqrt{Dt} \). To exclude this possibility, the Forward-Difference method is applied in Appendix H to a well-defined case which has no problem with these drawbacks. As verified, the observations of this study do not arise from these two weak points of the specific bulk diffusion problem that was selected for analysis.

In passing to a conclusion, there is one additional question to be answered. When, the results of Fig. 5.1, \( x \) equals \( \sqrt{2Dt} \) \((=1.44\sqrt{Dt})\) the Forward-Difference method becomes very accurate no matter what value of \( \lambda \) is used.

To confirm this observation, the Forward-Difference analysis has been performed using \( 8\sqrt{Dt} \) as a total length of \( x \) axis and \( 0.08\sqrt{Dt} \) as \( \Delta x \). The results are shown in Fig. 5.6. The same tendency as found in Fig. 5.1 may be seen, except that the magnitude of the error is larger than that of Fig. 5.1. This occurs because the value of \( \Delta x \) is larger than that used to obtain the result of Fig. 5.1. Why, then, does the Forward-Difference method become so accurate when \( x \) equals \( \sqrt{2Dt} \)? A random walk analysis can confirm that this value is the root-mean-square of the absolute distance from the origin[114];
Fig. 5.6 The variation of error between an analytic solution and the Forward-Difference method as a function of $x$ with various $\lambda$ values when different $\Delta x (= 0.08\sqrt{Dt})$ and different total length ($= 8\sqrt{Dt}$) are used.
where $x$ is the migration distance of diffusant from the origin.

Random work is certainly a combination of discrete jump steps in agreement with the characteristics of the Forward-Difference method. This supports the expectation that the Forward-Difference method should be accurate at this $x$ value no matter what value of $\lambda$ is used.
5.4 Summary

The Forward-Difference method and the Crank-Nicolson method were carefully applied to the diffusion equation which has a constant surface-concentration boundary condition for a semi-infinite medium, in which there is initially no concentration of diffusant in the medium. This is the situation which is often employed in bulk diffusion experiments. After applying the Forward-Difference method with various values of $\lambda$, it is found that, at a certain $\lambda$ value ($=1/6$), there is no noticeable error in the Forward-Difference method. This is connected to the characteristics of atomistic diffusion. On the other hand the Crank-Nicolson method has no advantage over the Forward-Difference method in this $\lambda$ range, $0.001 \leq \lambda \leq 0.4$.

This study confirms that the Forward-Difference method is a very accurate method in the range $0.001 \leq \lambda \leq 0.4$. It can be applied to any bulk diffusion study with complicated boundary or initial conditions to predict diffusion behavior with little significant error. This Finite Difference Method is an especially powerful tool in case of a finite medium. This is a situation often encountered in doing diffusion experiments, and for which solution of the diffusion equation to obtain an analytical solution is very time consuming if not an impossible task.
Chapter VI

Conclusions & Suggestions for Future Research

6.1 Summary of Results

1) Ultra high purity NiO bicrystals, probably of the highest quality produced to date, have been successfully grown by a CVT method using single crystals of MgO as substrates and HCl gas as a carrying agent. The epitaxially-grown bicrystals commonly displayed facets along the growth direction whose reflectivity suggests a small mosaic spread and good mechanical perfection. Chemical analysis of these crystals revealed the presence of no element at concentrations above their individual detection limits. By dissolving away the MgO substrate, free standing NiO crystals or bicrystals could be prepared. The thermodynamics of CVT process of NiO growth was described in so far as possible as an aid to establishing suitable growth parameters.

2) The accuracy of Le Claire's equation for obtaining a grain boundary diffusion product $aD'$ from a diffusion depth profile was examined within full range of diffusion parameters that constitute practical experiments. It has been shown that the method is not accurate over this entire range. Numerical integration was used to establish a superior equation obtaining grain boundary diffusion products from diffusion depth profiles to within an

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accuracy of 1%. The method, moreover, can be used in the design of appropriate diffusion experiments in advance unlike the Le Claire equation. In the latter method the results of an experiment can only be used after the fact to determine whether the experiment fell within the range of conditions for which Le Claire's analysis is valid.

3) The contribution of a space charge region to grain boundary diffusion was quantitatively investigated by solving 2-dimensional diffusion equations with the help of the FDM (Finite Difference Method). From the result of this study, the contribution of the space charge region to enhanced diffusion along the grain boundary could be directly calculated provided the potential in the bulk material and the dielectric constant are known. Application of the new relation for extraction of grain boundary diffusion products $aD'$ from concentration gradients allowed description of the gradient in terms of an effective value of $aD'$ for the slab of uniform fixed diffusivity in terms of which boundary transport is usually modelled.

4) In an attempt to be able to predict bulk diffusion behavior in solid subject to complex boundary and initial conditions, the FDM was applied to several model bulk diffusion problems. Among several analytic methods examined, the Forward-Difference method has displayed a very interesting behavior in terms of the relation between accuracy and the computational parameters selected for the analysis. This behavior could be successfully interpreted in terms of the physical nature of the diffusional process.
6.2 Suggestions for Future Research

Although we have achieved several significant separate results related to grain boundary diffusion, the final experimental determination of oxygen self-diffusion along a grain boundaries in NiO could not be accomplished. This was due to the technical problems within the Center for Materials Science and Engineering at MIT as this work was nearing completion, namely the untimely and unfortunate demise of our SIMS operator John Martin upon whom effective use of the instrument so heavily depended. It is thus truly desirable to perform in the near future grain boundary diffusion experiments using the well-characterized bicrystals(Chapter II). Since this crystal is ultra-high pure material, there is a good prospect that the intrinsic structure-property relations of grain boundary diffusion may be expected to be seen. From the diffusion depth profile which can be obtained with the aid of a SIMS experiment, an accurate grain boundary diffusion coefficient can now be determined by the method of Chapter III. This grain boundary diffusion coefficient will have significance in two respects. Firstly, it will be a true intrinsic grain boundary diffusion coefficient thanks to ultra high-purity of crystal and control of crystallography of the boundary. Secondly, the value of the grain boundary diffusion coefficient will be very accurate, without error greater than 1% as a consequence of an improved relation for the analysis of diffusion depth profiles.

Since we have developed a quantitative relationship for evaluation of the contribution of a space charge region to grain boundary diffusion(Chapter IV),
the effect of charge distribution at the grain boundary on the grain boundary diffusion should be studied. From these two studies, structural contribution of the grain boundary to the enhanced diffusion can be possibly separated from the data obtained in a grain boundary diffusion experiment. Those attempts will truly be the first step toward understanding the structure-property relationship for specific grain boundaries.
Appendix A

Derivation of Whipple's Exact Solution, Eqn. (3.8)

A.1 Diffusion Equation Describing Grain Boundary Diffusion.

The derivation of Whipple's exact solution, Eqn. (3.8), for grain boundary diffusion requires a great deal of mathematics even though the final result remains in an integral form rather than an analytical form. The more frustrating thing in the Whipple's original paper* is that its development is not self evident. In my individual experience, it took several weeks to understand the mathematics and fill the gaps of derivation. In this appendix a complete process of derivation of Whipple's exact solution is presented which makes the derivation more complete and self evident.

As described in Chapter III, it is necessary to consider two different coupled 2-dimensional diffusion equations to describe diffusion behavior of solute in a sample with a grain boundary (see Fig. 3.1 and text). First, in the grain boundary there is one diffusion equation,

---

\[
D' \left( \frac{\partial^2 C'}{\partial x^2} + \frac{\partial^2 C'}{\partial y^2} \right) = \frac{\partial C'}{\partial t} \quad \text{(A.1)}.
\]

In the bulk region there is another diffusion equation for solute,

\[
D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) = \frac{\partial C}{\partial t} \quad \text{(A.2)}.
\]

Corresponding boundary conditions are

\[
C' (\pm a, y, t) = C(\pm a, y, t) \quad \text{(A.3)},
\]

\[
D' \frac{\partial C'}{\partial x} (\pm a, y, t) = D \frac{\partial C}{\partial x}(\pm a, y, t) \quad \text{(A.4)},
\]

\[
C(x, 0, t) = C_S \quad \text{(A.5)},
\]

and

\[
C(x, \infty, t) = C_0 \quad \text{(A.6)}.
\]

An initial condition is

\[
C(x, y, 0) = C_0 \quad \text{(A.7)}.
\]

Since \( C' \) should be an even function along \( x \) axis and \( a \) is very small, \( C' \) can be approximated as follows within the grain boundary;

\[
C' (x, y, t) = C'_0 (y, t) + \frac{x^2}{2} C'_2 (y, t) \quad \text{(A.8)}.
\]
Then Eqn. (A.1) becomes

\[ D' \left[ C_2' + 2x \frac{\partial C_2'}{\partial x} + \frac{x^2}{2} \frac{\partial^2 C_2'}{\partial x^2} + \frac{\partial^2 C_0'}{\partial y^2} + \frac{x^2}{2} \frac{\partial^2 C_2'}{\partial y^2} \right] = \frac{\partial C_0'}{\partial t} + \frac{x^2}{2} \frac{\partial C_2'}{\partial t} \]  

(A.9).

Since \( x \) is very small in the grain boundary, Eqn (A.9) can be simplified as follows;

\[ D' \left[ C_2'(y,t) + \frac{\partial^2 C_0'(y,t)}{\partial y^2} \right] = \frac{\partial C_0'(y,t)}{\partial t} \]  

(A.10).

Using the boundary conditions, Eqns. (A.3) and (A.4), Eqn. (A.10) can be expressed as a function of \( C(x,y,t) \).

From Eqns. (A.3) and (A.8)

\[ C_0'(y,t) + \frac{a^2}{2} C_2'(y,t) = C(a,y,t) \]  

(A.11).

Using the fact that a half grain boundary width, \( a \), is very small, Eqn. (A.11) can be approximated as,

\[ C_0'(y,t) = C(a,y,t) \]  

(A.12).

From Eqns. (A.4) and (A.8),

\[ D' \left. \frac{\partial C'}{\partial x} \right|_{x=a} = D' \left[ x C_2'(y,t) \right]_{x=a} = D \left. \frac{\partial C}{\partial x} \right|_{x=a} \]
\[ \Rightarrow D' C'_2 = \frac{D}{a} \frac{\partial C}{\partial x} \bigg|_{x=a} \quad (A.13). \]

Substituting Eqns. (A.12) and (A.13) into Eqn. (A.10),

\[ D' \frac{\partial^2 C}{\partial y^2} + \frac{D}{a} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (at \ x = a) \quad (A.14). \]

Equation (A.2) can be expressed as

\[ \frac{\partial^2 C}{\partial y^2} = \frac{1}{D} \frac{\partial C}{\partial t} - \frac{\partial^2 C}{\partial x^2} \quad (A.15). \]

Substituting Eqn. (A.15) into (A.14) to get rid of \( y \) in Eqn. (A.14),

\[ D \frac{\partial^2 C}{\partial x^2} - \frac{D}{a} \frac{\partial C}{\partial x} = \left( \frac{D'}{D} - 1 \right) \frac{\partial C}{\partial t} \quad (at \ x = a) \quad (A.16). \]

What has been done so far can be summarized as follows;
Outside the grain boundary region \( C(x,y,t) \) can be described by using Eqn. (A.2), boundary condition Eqns. (A.16), (A.5), and (A.6), and an initial condition Eqn. (A.7). Originally it was necessary to solve two different partial differential equations, Eqn. (A.1) and Eqn. (A.2), with four boundary conditions, Eqns. (A.3)~(A.6), and one initial condition, Eqn (A.7), for grain boundary diffusion. However, after having made one assumption, namely that \( a \) is a very small quantity, the problem has been greatly simplified and reduced to the need to solve one partial differential equation, three boundary conditions, and one initial condition.
For convenience in the following derivation, \( C^* (x, y, t) \) is used instead of \( C(x, y, t) \).

\[
C^* (x, y, t) = C(x, y, t) - C_0
\]  

(A.17)

Then Eqn. (A.2) becomes

\[
D \nabla^2 C^* = \frac{\partial C^*}{\partial t}
\]  

(A.18).

Corresponding boundary conditions and initial condition are as follows (From Eqn. (A.16), Eqn. (A.5), Eqn. (A.6), and Eqn. (A.7));

\[
D \frac{\partial^2 C^*}{\partial x^2} - \frac{D}{a} \frac{\partial C^*}{\partial x} = \left( \frac{D'}{D} - 1 \right) \frac{\partial C^*}{\partial t} \text{ (at } x = a) \]  

(A.19),

\[
C^*(x, 0, t) = C_S - C_0 \]  

(A.20),

\[
C^*(x, \infty, t) = 0 \]  

(A.21),

\[
C^*(x, y, 0) = 0 \]  

(A.22).

First \( C^* (x, y, t) \) is obtained by solving Eqn. (A.18) with Eqns. (A.19), (A.20), (A.21), and (A.22). An expression for \( C(x, y, t) \) can then be later obtained by Eqn. (A.17).
A.2 Solving Eqn. (A.18) by Fourier-Laplace Transformation

A.2.1 Fourier-Laplace transformation of Eqn. (A.18)

As may be seen, Eqn. (A.18) is a two-dimensional partial differential equation which is almost impossible to solve explicitly. People normally solve partial differential equations by Fourier and Laplace transformation. For the present problem this means the use of the Laplace transformation for the time axis and Fourier transformation for one of spatial axes, e.g. the x axis or y axis. Transformation gives simplicity in solving partial diffusion equations.

Application of Fourier-Laplace transformation to Eqn. (A.18) involves use of the relation

$$\psi(x,\mu,\lambda) = \int_0^\infty \exp(-\lambda t) dt \int_0^\infty \sin(\mu y) C^* (x,y,t) dy$$

(A.23).

The transformation equation, Eqn. (A.23), is applied to both sides of Eqn. (A.18).

$$\int_0^\infty dt \int_0^\infty dy \frac{\partial^2 C^*}{\partial x^2} e^{-\lambda t} \sin(\mu y)$$

$$= \frac{\partial^2}{\partial x^2} \int_0^\infty dt \int_0^\infty dy C^* (x,y,t) e^{-\lambda t} \sin(\mu y)$$

$$= \frac{\partial^2 \psi}{\partial x^2}$$

(A.24),
\[
\int_0^\infty dt \int_0^\infty dy \frac{\partial^2 C^*}{\partial y^2} e^{(-\lambda t)} \sin(\mu y)
\]

\[
= \int_0^\infty dt e^{(-\lambda t)} \int_0^\infty dy \frac{\partial^2 C^*}{\partial y^2} \sin(\mu y)
\]

\[
= \int_0^\infty dt e^{(-\lambda t)} \left[ \sin(\mu y) \frac{\partial C^*}{\partial y} \bigg|_0^\infty - \left( \mu \cos(\mu y) C^* \bigg|_0^\infty + \int_0^\infty dy \mu^2 \sin(\mu y) C^* \right) \right]
\]

\[
= \frac{\partial C^*}{\partial y} \bigg|_{y=\infty} = 0 \quad \text{and Eqns. (A.20), (A.21)}
\]

\[
= \int_0^\infty dt e^{(-\lambda t)} \left[ \mu (C_S - C_0) - \mu^2 \int_0^\infty dy \sin(\mu y) C^* \right]
\]

\[
= \frac{\mu}{\lambda} (C_S - C_0) - \mu^2 \psi
\]

(A.25),

and

\[
\int_0^\infty dy \int_0^\infty dt \frac{\partial C^*}{\partial t} e^{(-\lambda t)} \sin(\mu y)
\]

\[
= \int_0^\infty dy \sin(\mu y) \int_0^\infty dt \frac{\partial C^*}{\partial t} e^{(-\lambda t)}
\]

\[
= \int_0^\infty dy \sin(\mu y) \left[ C^* e^{(-\lambda t)} \bigg|_0^\infty + \int_0^\infty dt \lambda e^{(-\lambda t)} C^* \right]
\]

\[
= \text{Eqn. (A.22)}
\]

\[
= \int_0^\infty dy \sin(\mu y) \left[ \int_0^\infty dt \lambda e^{(-\lambda t)} C^* \right]
\]

\[
= \lambda \psi
\]

(A.26).

From Eqns. (A.24)–(A.26), the Fourier-Laplace transformation of Eqn. (A.18) has the form
\[
\frac{\partial^2 \psi}{\partial x^2} - \left[ \mu^2 + \frac{\lambda}{D} \right] \psi = -\frac{\mu}{\lambda} (C_s - C_0)
\]  
(A.27).

The corresponding boundary condition can be obtained by applying Fourier-Laplace transformation to Eqn. (A.19).

\[
D' \int_0^\infty dt \int_0^\infty dy \frac{\partial^2 C^*}{\partial x^2} e^{(-\lambda t)} \sin(\mu y)
\]

\[
= D \frac{\partial^2 \psi}{\partial x^2}
\]  
(A.28),

\[
= D \frac{\partial}{\partial x} \left[ \int_0^\infty dt \int_0^\infty dy C^* e^{(-\lambda t)} \sin(\mu y) \right]
\]

\[
= -\frac{D}{a} \int_0^\infty dt \left[ \int_0^\infty dy C^* e^{(-\lambda t)} \sin(\mu y) \right]
\]

\[
= -\frac{D}{a} \frac{\partial \psi}{\partial x}
\]  
(A.29),

and

\[
\left( \frac{D'}{D} - 1 \right) \int_0^\infty dy \int_0^\infty dt \frac{\partial C^*}{\partial t} e^{(-\lambda t)} \sin(\mu y)
\]

\[
= \left( \frac{D'}{D} - 1 \right) \int_0^\infty dy \sin(\mu y) \int_0^\infty dt \frac{\partial C^*}{\partial t} e^{(-\lambda t)}
\]

\[
= \left( \frac{D'}{D} - 1 \right) \int_0^\infty dy \sin(\mu y) \left[ C^* e^{(-\lambda t)} \bigg|_0^\infty + \int_0^\infty dt \lambda e^{(-\lambda t)} C^* \right]
\]

\[
\Leftrightarrow \quad \text{Eqn. (A.22)}
\]
From Eqns. (A.28)-(A.30), the transformed boundary condition is

\[ D' \frac{d^2 \psi}{dx^2} - \frac{D}{a} \frac{d \psi}{dx} - \left( \frac{D'}{D} - 1 \right) \lambda \psi = 0 \quad (at \ x = a) \quad (A.31). \]

A.2.2. Solving the differential equation, Eqn. (A.27) with Eqn. (A.31)

Since Eqn. (A.27) is an inhomogeneous second-order differential equation, it can be easily recognized that solution of Eqn. (A.27) consists of a general solution, \( \psi_g \), and a particular solution, \( \psi_p \).

\[ \psi = \psi_g + \psi_p \quad (A.32) \]

The general solution is

\[ \psi_g = C_1 e^{-\sqrt{\left(\frac{\mu^2 + \lambda}{D}\right)x}} + C_2 e^{\sqrt{\left(\frac{\mu^2 + \lambda}{D}\right)x}} \quad (A.33). \]

The particular solution is

\[ \psi_p = C_3 x^2 + C_4 x + C_5 \quad (A.34). \]
The constants in Eqn. (A.34) can be determined easily by substituting into Eqn. (A.27).

\[ C_3 = 0 \quad , \quad C_4 = 0 \quad , \quad C_5 = \frac{\mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)} (C_S - C_0) \]

The particular solution is then

\[ \psi_p = \frac{\mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)} (C_S - C_0) \] (A.35).

From Eqn. (A.32) and Eqn. (A.35), Eqn. (A.32) becomes

\[ \psi = C_1 e^{-\sqrt{\left( \mu^2 + \frac{\lambda}{D} \right)x}} + C_2 e^{\sqrt{\left( \mu^2 + \frac{\lambda}{D} \right)x}} + \frac{\mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)} (C_S - C_0) \] (A.36).

When \( x \to \infty \), \( \psi \) should be finite. It means that \( C_2 \) of Eqn. (A.36) should be zero at \( x \to \infty \).

\[ \psi = C_1 e^{-\sqrt{\left( \mu^2 + \frac{\lambda}{D} \right)x}} + \frac{\mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)} (C_S - C_0) \] (A.37)

From the boundary condition, Eqn. (A.31), \( C_1 \) could be determined as
\[ C_1 = \frac{(C_S - C_0) \left( \frac{D}{D} - 1 \right) \mu e^{\frac{\sqrt{\mu^2 + \frac{\lambda}{D}}}{a}}}{\left( D \mu^2 + \frac{D}{a} \right) \left( \mu^2 + \frac{\lambda}{D} \right) + \lambda} \]  

(A.38).

Substituting Eqn. (A.38) into Eqn. (A.37) gives

\[
\psi(x,\mu,\lambda) = \frac{(C_S - C_0) \left( \frac{D}{D} - 1 \right) \mu e^{\frac{\sqrt{\mu^2 + \frac{\lambda}{D}}}{a}}}{\left( D \mu^2 + \frac{D}{a} \right) \left( \mu^2 + \frac{\lambda}{D} \right) + \lambda} + \frac{\mu}{\lambda} \left( C_S - C_0 \right)
\]

(A.39).

Next step of derivation is an inverse Fourier-Laplace transformation. For convenience in derivation, \( \psi \) is written as follows,

\[
\psi(x,\mu,\lambda) = \psi_1(x,\mu,\lambda) + \psi_2(x,\mu,\lambda)
\]

(A.40)

where

\[
\psi_1(x,\mu,\lambda) = \frac{(C_S - C_0) \left( \frac{D}{D} - 1 \right) \mu e^{\frac{\sqrt{\mu^2 + \frac{\lambda}{D}}}{a}}}{\left( D \mu^2 + \frac{D}{a} \right) \left( \mu^2 + \frac{\lambda}{D} \right) + \lambda}
\]

(A.41),

and

\[
\psi_2(x,\mu,\lambda) = \frac{\mu}{\lambda} \left( C_S - C_0 \right)
\]

(A.42).
A.2.3 Inverse Fourier-Laplace transformation of Eqn. (A.40)

To go back to $C^*(x,y,t)$ from $\psi(x,\mu,\lambda)$ an inverse Fourier-Laplace transformation is performed on Eqn. (A.40).

\[
C^*(x,y,t) = \frac{1}{\pi} \int_{-\infty}^{\infty} \sin(\mu y) d\mu \quad \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \exp(\lambda t) \psi(x,\mu,\lambda) d\lambda
\]  
(A.43)

\[
= C_1^*(x,y,t) + C_2^*(x,y,t)
\]

where

\[
C_1^*(x,y,t) = \frac{1}{\pi} \int_{-\infty}^{\infty} \sin(\mu y) d\mu \quad \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \exp(\lambda t) \psi_1(x,\mu,\lambda) d\lambda
\]  
(A.44),

and

\[
C_2^*(x,y,t) = \frac{1}{\pi} \int_{-\infty}^{\infty} \sin(\mu y) d\mu \quad \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \exp(\lambda t) \psi_2(x,\mu,\lambda) d\lambda
\]  
(A.45).

From Eqn. (A.45) and Eqn. (A.42)

\[
C_2^*(x,y,t) = \frac{1}{\pi} \int_{-\infty}^{\infty} \sin(\mu y) d\mu \quad \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \exp(\lambda t) \left( \frac{C_s-C_0}{\lambda} \right) d\lambda
\]  
(A.46).

In Eqn. (A.46)
\[
\frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \exp(\lambda t) \frac{(C_S - C_0) \mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)} d\lambda = (C_S - C_0) \frac{1 - \exp(-\mu^2 D t)}{\mu}
\]

(A.47).

Equation (A.47) comes from the inverse Laplace transformation of \( \frac{(C_S - C_0) \mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)} \).

Then

\[
C_2 * (x, y, t) = (C_S - C_0) \frac{1}{\pi} \int_{-\infty}^{\infty} \sin(\mu y) \frac{1 - \exp(-\mu^2 D t)}{\mu} d\mu
\]

(A.48).

Let \( v = \mu y \),

\[
C_2 * (x, y, t) = (C_S - C_0) \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\sin(v)}{v} \left[ 1 - \exp\left( -\frac{v^2 D t}{y^2} \right) \right] dv
\]

\[
= (C_S - C_0) \left\{ \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\sin(v)}{v} dv - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\sin(v)}{v} \exp\left( -\frac{v^2 D t}{y^2} \right) dv \right\}
\]

\[
= (C_S - C_0) \left[ 1 - \text{erf}\left( \frac{y}{2\sqrt{D} t} \right) \right]
\]

\[
= (C_S - C_0) \text{erfc}\left( \frac{y}{2\sqrt{D} t} \right)
\]

(A.49).

Before doing the calculation of Eqn. (A.44), let \( \mu' = \mu \sqrt{D} t \) and \( \lambda' = \lambda t \) in Eqn. (A.41).
\[
\psi_1(x, \mu', \lambda') = \frac{(C_S - C_0)(\Delta - 1) \frac{\Delta t^2}{\Delta t} e^{-\frac{\sqrt{\mu'^2 + \lambda}}{\Delta t}}}{\left(\Delta \mu'^2 + \frac{1}{\alpha} \sqrt{\mu'^2 + \lambda'} + \lambda'\right)(\mu'^2 + \lambda')}(x-a)
\]

(A.50)

where

\[
\Delta = \frac{D'}{D}
\]

(A.51),

and

\[
\alpha = \frac{a}{\sqrt{\Delta t}}
\]

(A.52).

Equation (A.44) then becomes

\[
C_1 \ast (x, y, t) = (C_S - C_0) \frac{\Delta - 1}{2 \pi i} \int_{-\infty}^{\infty} \sin(\mu' \eta) \mu' d\mu'
\]

\[
\times \int_{-\infty}^{\infty} d\lambda' \cdot \frac{\exp\left[\lambda' - \left(\frac{\mu'^2 + \lambda'}{\xi}\right)\right]}{\left(\mu'^2 + \lambda'\right)\left(\Delta \mu'^2 + \frac{1}{\alpha} \sqrt{\mu'^2 + \lambda'} + \lambda'\right)}
\]

(A.53)

where

\[
\eta = \frac{y}{\sqrt{\Delta t}}
\]

(A.54),

and

\[
\xi = \frac{x-a}{\sqrt{\Delta t}}
\]

(A.55).
If \( \lambda' = v^2 - \mu'^2 \), in Eqn. (A.53)

\[
\int_{-i\infty}^{i\infty} d\lambda' \frac{\exp[\lambda' - \sqrt{\left(\mu'^2 + \lambda'\right)\xi}]}{\left(\mu'^2 + \lambda'\right) \Delta \mu'^2 + \frac{1}{\alpha} \sqrt{\left(\mu'^2 + \lambda'\right) + \lambda'}}
\]

\[
= 2 \exp(-\mu'^2) \int_{-i\infty}^{i\infty} \frac{\exp\left(v^2 - v \xi\right)}{(\Delta - 1)\mu'^2 + v + \frac{v^2}{\Delta - 1}} \, dv.
\]

Then

\[
C_1^* (x,y,t) = \frac{\left(C_S - C_0\right)}{\pi^2 i} \int_{-\infty}^{\infty} \sin(\mu' \eta) \exp(-\mu'^2) \mu' \, d\mu'
\]

\[
\times \int_{-i\infty}^{i\infty} \frac{\exp\left(v^2 - v \xi\right)}{\mu'^2 + v + \frac{v^2}{\Delta - 1}} \frac{dv}{v} \tag{A.56}
\]

where

\[
\beta = \alpha (\Delta - 1) \tag{A.57}
\]

Several mathematical equivalents have been used to make Eqn. (A.56) more accessible.

They are

\[
\mu' \sin(\mu \eta) = -\frac{1}{2} \frac{\partial}{\partial \eta} \left[ \exp(i \mu \eta) + \exp(-i \mu \eta) \right] \tag{A.58},
\]

\[
\frac{\exp(-v \xi)}{v} = \int_{\xi}^{\infty} \exp(-v \xi') \, d\xi' \tag{A.59},
\]
and
\[
\frac{1}{\mu^2 + \nu + \frac{\nu^2}{\Delta - 1}} = \exp\left(\mu^2 + \nu + \frac{\nu^2}{\Delta - 1}\right) \int_{1}^{\infty} d\sigma \exp\left[-\left(\mu^2 + \nu + \frac{\nu^2}{\Delta - 1}\right)\sigma\right]
\]  \hspace{1cm} (A.60).

Substituting Eqns. (A.58), (A.59), and (A.60) into Eqn. (A.56),
\[
C_1^* = -\frac{(C_S - C_0)}{2} \frac{\partial}{\partial \eta} \int_{\xi}^{\infty} d\xi' \int_{1}^{\infty} d\sigma \frac{1}{\pi} \int_{-\infty}^{\infty} \left[\exp(i\mu\eta - \mu^2 \sigma) + \exp(-i\mu\eta - \mu^2 \sigma)\right] d\mu' \times \frac{1}{\pi i} \int_{-\infty}^{\infty} \exp\left[i\eta \xi + \sigma - 1\right] d\nu
\]  \hspace{1cm} (A.61).

Here
\[
\int_{-\infty}^{\infty} \exp\left(i\mu\eta - \mu^2 \sigma\right) d\mu = \int_{-\infty}^{\infty} \exp\left(-i\mu\eta - \mu^2 \sigma\right) d\nu
\]  \hspace{1cm} (A.62).

And if \(\nu = z \imath\), then
\[
\frac{1}{\pi i} \int_{-\infty}^{\infty} \exp\left[i\eta \xi + \sigma - 1\right] d\nu = \frac{1}{\pi} \int_{-\infty}^{\infty} \exp\left[-z^2 \frac{\Delta - \sigma}{\Delta - 1} - iz\left(\xi + \frac{\sigma - 1}{\beta}\right)\right] dz
\]  \hspace{1cm} (A.63).
Substituting Eqns. (A.62) and (A.63) into Eqn. (A.61)

\[
C_1^* = -\frac{C_S - C_0}{\pi} \frac{\partial}{\partial \eta} \int_1^\infty \frac{d\sigma}{\sqrt{\sigma}} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \int_\xi^\infty d\xi' \exp\left(-\frac{1}{4} \left(\frac{\Delta - 1}{\Delta - \sigma}\right) \left(\xi' - \frac{\sigma - 1}{\beta}\right)^2\right)
\]

(A.64).

Using

\[
\frac{\partial}{\partial \eta} \left\{ \exp\left(-\frac{\eta^2}{4\sigma}\right) \right\} = -\frac{\eta}{2\sigma} \exp\left(-\frac{\eta^2}{4\sigma}\right)
\]

and

\[
\int_\xi^\infty d\xi' \exp\left[-\frac{1}{4} \left(\frac{\Delta - 1}{\Delta - \sigma}\right) \left(\xi' - \frac{\sigma - 1}{\beta}\right)^2\right] = \sqrt{\frac{\Delta - \sigma}{\Delta - 1}} \sqrt{\pi} \text{erfc}\left[\frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \left(\xi + \frac{\sigma - 1}{\beta}\right)\right]
\]

(A.66),

Eqn. (A.64) becomes

\[
C_1^* = (C_S - C_0) \frac{\eta}{2\sqrt{\pi}} \frac{\partial}{\partial \eta} \int_1^\infty \frac{d\sigma}{\sigma^{1/2}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \text{erfc}\left[\frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \left(\xi + \frac{\sigma - 1}{\beta}\right)\right]
\]

(A.67)

where the definitions of parameters have been given in Eqns. (A.51), (A.52), (A.54), (A.55), and (A.57).

Finally, from Eqns. (A.17), (A.43), (A.49), and (A.67), \(C(x,y,t)\) may be obtained as

\[
C(x,y,t) = C_0 + (C_S - C_0) \text{erfc}\left(\frac{y}{2\sqrt{Dt}}\right) \]

\[
+ (C_S - C_0) \frac{\eta}{2\sqrt{\pi}} \frac{\partial}{\partial \eta} \int_1^\infty \frac{d\sigma}{\sigma^{1/2}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \text{erfc}\left[\frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \left(\xi + \frac{\sigma - 1}{\beta}\right)\right]
\]

(A.68)

where \(\Delta = \frac{D}{D}, \eta = \frac{y}{\sqrt{Dt}}, \xi = \frac{x-a}{\sqrt{Dt}}, \) and \(\beta = (\Delta - 1) \frac{a}{\sqrt{Dt}}.\)
A.3 Sectioning Experiment

In performing a sectioning experiment such as SIMS sputtering to obtain the depth profile of diffusant in a sample, only an average concentration profile (along x axis in this case) of diffusant is usually obtained. If $L$ is defined as a half width along the x axis of the scanning range of the SIMS sputtering experiment, the average concentration, $\bar{C}(x,y,t)$, has the form

$$\bar{C}(y,t) = \frac{\int_0^L C(x,y,t) \, dx}{\int_0^L dx}$$

(A.69).

And since $a$ is very small compared to $L$,

$$\bar{C}(y,t) = \frac{\int_a^L C(x,y,t) \, dx}{\int_0^L dx} = \frac{\int_a^L C(x,y,t) \, dx}{L} = C_0 + \bar{C}_1 + \bar{C}_2$$

(A.70)

where

$$\bar{C}_1 = \frac{1}{L} \int_a^L dx (C_S - C_0) \frac{\eta}{2\sqrt{\pi}} \int_1^\infty \frac{d\sigma}{\sigma} \exp\left(-\frac{\eta^2}{4\sigma}\right) \text{erfc}\left[\frac{1}{2}\sqrt{\frac{\Delta-1}{\Delta-\sigma}} \left(\xi + \frac{\sigma-1}{\beta}\right)\right]$$

(A.71)

and

$$\bar{C}_2 = \frac{1}{L} \int_a^L dx (C_S - C_0) \text{erfc}\left(\frac{y}{2\sqrt{Dt}}\right)$$

(A.72).

Using

$$\int_a^L \text{erfc}\left[\frac{1}{2}\sqrt{\frac{\Delta-1}{\Delta-\sigma}} \left(\xi + \frac{\sigma-1}{\beta}\right)\right] dx$$
\[ \bar{C}_1^* \text{ can be written as} \]
\[ \bar{C}_1^* = (C_S - C_0) \frac{y}{L \sqrt{\pi}} \int_1^\infty \frac{d\sigma}{\sigma^{3/2}} \exp \left( -\frac{\eta^2}{4\sigma} \right) \frac{\Delta - \sigma}{\Delta - 1} \times \left\{ \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1 - \sigma}{\Delta - \beta}} \right] - \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sqrt{Dt} + \sigma - 1}} \right] \right\} \]

(A.73).

\[ \bar{C}_2^* \text{ is} \]
\[ \bar{C}_2^* = (C_S - C_0) \text{erfc} \left( \frac{y}{2\sqrt{Dt}} \right) \]

(A.74).

Finally,
\[ \frac{\bar{C}(y,t) - C_0}{C_S - C_0} = \left[ \frac{y}{L \sqrt{\pi}} \int_1^\infty \frac{d\sigma}{\sigma^{3/2}} \exp \left( -\frac{\eta^2}{4\sigma} \right) \frac{\Delta - \sigma}{\Delta - 1} \right] \times \left\{ \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1 - \sigma}{\Delta - \beta}} \right] - \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sqrt{Dt} + \sigma - 1}} \right] \right\} \\
+ \text{erfc} \left( \frac{y}{2\sqrt{Dt}} \right) \]

(A.73)

where \( \Delta = \frac{D}{D^*} \), \( \eta = \frac{y}{\sqrt{Dt}} \), and \( \beta = (\Delta - 1) \frac{a}{\sqrt{Dt}} \).
Appendix B

Numerical Integration of Eqn. (3.21) and Eqn. (3.22)

B.1 Setting the upper bound of numerical integration

Numerical integration of \( I_1 \) and \( I_2 \),

\[
I_1 = \left[ \int_1^{\infty} \frac{\partial \sigma}{\sigma^{1.5}} \exp \left( -\frac{\eta^2}{4\sigma} \right) \text{erfc} \left( \frac{1}{2} \frac{\sigma - 1}{\beta} \right) \right] \tag{3.21}
\]

and

\[
I_2 = \left[ \int_1^{\infty} \frac{\partial \sigma}{\sigma^{2.5}} \exp \left( -\frac{\eta^2}{4\sigma} \right) \text{erfc} \left( \frac{1}{2} \frac{\sigma - 1}{\beta} \right) \right] \tag{3.22}
\]

requires integration from 1 to infinity. However, it is not possible to introduce the concept of infinity in the numerical integration procedure. It is required that a reasonable end point of numerical integration be established. In Fig. B.1 the integrands of \( I_1 \) and \( I_2 \) are plotted as a function of \( \sigma \) when \( \beta \) equals 10 and \( \eta \) equals 6. As shown, the integrands of \( I_1 \) and \( I_2 \) decay very rapidly. To see the degree of decay of the integrands of \( I_1 \) and \( I_2 \) graphically,
log plots of the integrands are shown in the accompanying Fig. B.2. Although $\sigma$ has been extended only to 100, the variation of these integrands is order 12 for $I_1$ and order 15 for $I_2$. This means that we can use an upper bound for the numerical integration of Eqns. (3.21) and (3.22) that is much less than 100. Essential range of $\sigma$ over which significant contributions are made to the value of the numerical integration can be established through the plotting the integrand for each $\beta$ and $\eta$. From each plot a reasonable upper bound for numerical integration could be obtained.

B.2. The Accuracy of Numerical Integration

Unfortunately, it is very hard to know the accuracy of a calculation when the numerical integration is done by the Mathematica program. There is no description in the manual on the method of numerical integration which is used when the numerical integration procedure is invoked. However, in any attempt to apply this program the accuracy of this numerical integration should be checked since improved reliability is one of the essential aspects claimed for the method which was developed in Chapter III.

The accuracy of numerical integration can be indirectly checked as follows; 1) Devise a function behaving similar to the integrands of $I_1$ and $I_2$, 2) Numerically integrate that function by the same routine in Mathematica program, 3) Compare this value with exact solution.

For this purpose following function was chosen,

$$f(x) = x^4 \exp \left( \frac{-x}{3} \right)$$

(B.1.)
The behavior of this function is shown in Fig. B.3. Its behavior looks very similar to the integrands of $I_1$ and $I_2$. Also, the log plot of Eqn. (B.1) shows that the degree of variation of this function is order 8, which means that it is an even more severe test of the truncation error.

Using the model function, $f(x)$, numerical integration is done by Mathematica in the range of $0 \sim 100$ as,

$$\int_{0}^{100} f(x)dx$$ \hspace{1cm} (B.2).

Numerical integration by Mathematica gives,

$$5831.99999866008751$$ \hspace{1cm} (B.3).

True value of integration obtained by exact integration is

$$5832 - 339440232 \exp\left(-\frac{100}{3}\right)$$ \hspace{1cm} (B.4).

$$= 5831.99999866867788$$

Surprisingly the error of numerical integration is

$$8.59037 \times 10^{-10}$$ \hspace{1cm} (B.5).

This suggests that the numerical integration routine in Mathematica is very accurate in doing numerical integration of functions behaving like $I_1$ and $I_2$. In addition, the integral value of $f(x)$ from 0 to infinity can be calculated easily since $f(x)$ is well behaved.
\[ \int_{0}^{\infty} f(x)dx = 5832 \quad \text{(B.6).} \]

This value certainly does not deviates much from the value of Eqn. (B.3) which comes from numerical integration of \( f(x) \) from 0 to 100. Setting the upper bound as 100 instead of infinity is reasonable for the present computations. This argument can be extended to numerical integration of \( I_1 \) and \( I_2 \) as well.
Fig. B.1 Behaviour of integrands of $I_1$ and $I_2$ as a function of $\sigma$ when $\beta$ equals 10 and $\eta$ equals 6, which shows a fast decay.
Fig. B.2 Logarithmically plotted integrands of $I_1$ and $I_2$ when $\beta$ equals 10 and $\eta$ equals 6.
Fig. B.3 Behaviour of $f(x)$ which was designed to predict the accuracy of numerical integration.
Appendix C

C.1 The effect of the value of L on Eqns. (3.19) and (3.20)

To check the effect of the value of L on Eqn. (3.19) and (3.20), \( \frac{\partial \ln C}{\partial \eta^{6/5}} \) is computed with inclusion of the term L, which is the half-width of the area sputtered by the primary ion beam in SIMS analysis.

\[
\left( \frac{\partial \ln C}{\partial \eta^{6/5}} \right)_{(L)} = \frac{I_{1(L)} - \eta^2}{2 \cdot \eta^{1.2} \cdot I_{2(L)}}
\]  

(C.1)

where

\[
I_{1(L)} = \left[ \int_{1}^{\infty} \frac{\partial \sigma}{\sigma^{1.5}} \exp \left( -\frac{\eta^2}{4\sigma} \right) \right] \\
\times \left\{ \text{erfc} \left[ \frac{1}{2} \frac{\sigma - 1}{\beta} \right] - \text{erfc} \left[ \frac{1}{2} \frac{L - a + \sigma - 1}{\sqrt{Dt} + \beta} \right] \right\}
\]  

(C.2)

and

\[
I_{2(L)} = \left[ \int_{1}^{\infty} \frac{\partial \sigma}{\sigma^{2.5}} \exp \left( -\frac{\eta^2}{4\sigma} \right) \right]
\times \left\{ \text{erfc} \left[ \frac{1}{2} \frac{\sigma - 1}{\beta} \right] - \text{erfc} \left[ \frac{1}{2} \frac{L - a + \sigma - 1}{\sqrt{Dt} + \beta} \right] \right\}
\]  

(C.3)
The results are then compared with \( \frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \) \( \text{(Eqn. (3.18))} \) using Eqns. (3.21) and (3.22), the approximate integrations, in which the term L has been eliminated. Figure C.1 shows that for all \( \beta \) values in the range of \( 6 \leq \eta \leq 20 \), the relative error in the approximate value of \( \frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \) is within 1% of the true value provided \( L \geq 4\sqrt{Dt} \).
Fig. C.1(a) The effect of the value of $L$ in $\frac{\partial \ln \bar{C}}{\partial \eta_{\delta/\delta}}$ when $\beta$ equals 1.
Fig. C.1(b) The effect of the value of $L$ in $\frac{\partial \ln C}{\partial \eta^{6/5}}$ when $\beta$ equals 10.
Fig. C.1(c) The effect of the value of $L$ in $\frac{\partial \ln \tilde{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 100.
Fig. C.1(d) The effect of the value of $L$ in $\frac{\partial \ln \overline{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 1000.
Fig. C.1(e) The effect of the value of $L$ in $\frac{\partial \ln \mathcal{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 10000.
Fig. C.1(f) The effect of the value of L in $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 100000.
C.2 The effect of the value of $\Delta$ on Eqns. (3.19) and (3.20)

The exact value of $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ is also computed with inclusion of the term, $\Delta = \frac{D'}{D}$.

\[
\left( \frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \right)_{(\Delta)} = \frac{I_{1(\Delta)} - \frac{\eta^2}{2} I_{2(\Delta)}}{1.2 \eta^{12} I_{1(\Delta)}}
\]

where
\[
I_{1(\Delta)} = \left[ \int_1^{\infty} \frac{\partial \sigma}{\sigma^{1/5}} \exp \left( \frac{-\eta^2}{4\sigma} \right) \sqrt{\frac{\Delta - \sigma}{\Delta - 1}} \times \left\{ \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \beta \right] \right\} \right]
\]

and
\[
I_{2(\Delta)} = \left[ \int_1^{\infty} \frac{\partial \sigma}{\sigma^{2/5}} \exp \left( \frac{-\eta^2}{4\sigma} \right) \sqrt{\frac{\Delta - \sigma}{\Delta - 1}} \times \left\{ \text{erfc} \left[ \frac{1}{2} \sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \beta \right] \right\} \right]
\]

The results of the integrations are compared in Fig. C.2 with the approximate value of $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ in which the $\Delta$ term was eliminated, that is, Eqns. (3.21) and (3.22). It is safe to say that for all $\beta$ values in the range of $6 \leq \eta \leq 20$, the relative error in the value of $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ is within 1% if $\frac{\Delta}{\beta} \geq 10^3$ or, in other terms if $\frac{\sqrt{Dr}}{a} \geq 10^3$. 

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Fig. C.2(a) The effect of the value of $\Delta$ in $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 1.
Fig. C.2(b) The effect of the value of $\Delta$ in $\frac{\partial \ln C}{\partial \eta^{6/5}}$ when $\beta$ equals 10.
Fig. C.2(c) The effect of the value of $\Delta$ in $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 100.
Fig. C.2(d) The effect of the value of \( \Delta \) in \( \frac{\partial \ln \bar{C}}{\partial \eta^{6/5}} \) when \( \beta \) equals 1000.
Fig. C.2(e) The effect of the value of $\Delta$ in $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 10000.
Fig. C.2(f) The effect of the value of $\Delta$ in $\frac{\partial \ln \bar{C}}{\partial \eta^{6/5}}$ when $\beta$ equals 100000.
Appendix D

Utilization of Two Different Grid Sizes in the Crank-Nicolson Method

When two different grid sizes are employed in defining intervals along the x axis, one point of concern is behavior at the locations where the two different sizes of grids meet each other-in other words, the position of $C_i$ in Fig. D.1.

Employing a Taylor expansion of the concentration up to second order,

$$C_{i+1} = C_i + h^2 \left( \frac{\partial C}{\partial x} \right)_i + \frac{1}{2} h^2 \left( \frac{\partial^2 C}{\partial x^2} \right)_i$$  \hspace{1cm} (D.1)

and

$$C_{i-1} = C_i - h^1 \left( \frac{\partial C}{\partial x} \right)_i + \frac{1}{2} h^1 \left( \frac{\partial^2 C}{\partial x^2} \right)_i$$  \hspace{1cm} (D.2).

From Eqn. (D.1) and (D.2)

$$\left( \frac{\partial C}{\partial x} \right)_i = \frac{h^2 C_{i+1} + \left( h^2 - h^2 \right) C_i - h^2 C_{i-1}}{h1h2(h1+h2)}$$  \hspace{1cm} (D.3)

and
\[
\left( \frac{\partial^2 C}{\partial X^2} \right)_i = \frac{h_1 C_{i+1} - (h_1 + h_2) C_i + h_2 C_{i-1}}{0.5h_1 h_2 (h_1 + h_2)} \quad (D.4).
\]

Using Eqn. (D.3) and (D.4), and the basic concept of the Crank-Nicolson method, which are

\[
\frac{\partial C}{\partial t} = \left( \frac{C_{k+1} - C_k}{l} \right)_{i,j} \quad (D.5)
\]

\[
\frac{\partial C}{\partial X} = \frac{1}{2} \left\{ \left( \frac{\partial C}{\partial X} \right)_{k+1} + \left( \frac{\partial C}{\partial X} \right)_k \right\} \quad (D.6)
\]

\[
\frac{\partial^2 C}{\partial X^2} = \frac{1}{2} \left\{ \left( \frac{\partial^2 C}{\partial X^2} \right)_{k+1} + \left( \frac{\partial^2 C}{\partial X^2} \right)_k \right\} \quad (D.7)
\]

and

\[
\frac{\partial^2 C}{\partial Y^2} = \frac{1}{2} \left\{ \left( \frac{\partial^2 C}{\partial Y^2} \right)_{k+1} + \left( \frac{\partial^2 C}{\partial Y^2} \right)_k \right\} \quad (D.8),
\]

two different grid sizes can be fit into the Crank-Nicolson method without any extra difficulty.
Fig. D.1 Schematic diagram which shows two different sizes of grid used in the Finite Difference Method for $x$ axis.
Appendix E

Results of Calculations of $C(x,y,t)$ under the Influence of Space Charge Adjacent to the Boundary (Chapter IV)

E.1 Computation of $C(x,y,t)$ using Hyperbolic Potential Term, Eqn. (4.6)

Followings are the result of the calculation of $C(x,y,t)$, Eqn. (4.22), using Eqn. (4.6) for various values of $\frac{z_i e \phi_{\infty}}{kT}$. 
Fig. E.1 Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \phi_\infty}{kT}$ equals 1.5.
Fig. E.2 Computed concentration distribution in a medium, \( C(x,y,t) \),
when \( \frac{z_i e \phi_{\infty}}{kT} \) equals 2.
Fig. E.3 Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z\epsilon\phi_{\infty}}{kT}$ equals 2.5.
Fig. E.4  Computed concentration distribution in a medium, \( C(x,y,t) \), when \( \frac{z_i e \phi_\infty}{kT} \) equals 3.
Fig. E.5  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \phi_\infty}{kT}$ equals 3.5.
Fig. E.6  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \phi_{\infty}}{kT}$ equals 4.
Fig. E.7  Computed concentration distribution in a medium, \( C(x,y,t) \), when \( \frac{z_i e \phi_\infty}{kT} \) equals 4.5.
Fig. E.8  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_{eff} \phi_{\infty}}{kT}$ equals 5.
E.2 Computation of $C(x,y,t)$ using Exponential Potential Term, Eqn. (4.42)

Followings are the result of the calculation of $C(x,y,t)$, Eqn. (4.22), using Eqn. (4.42) for various values of $\frac{z_i e \phi_{\infty}}{kT}$.
Fig. E.9  Computed concentration distribution in a medium, $C(x, y, t)$, when $\frac{z_f \phi_\infty}{kT}$ equals 1.5.
Fig. E.10  Computed concentration distribution in a medium, $C(x, y, t)$, when $\frac{z_i e \phi_\infty}{kT}$ equals 2.
Fig. E.11  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \Phi_\infty}{kT}$ equals 2.5.
Fig. E.12  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \Phi_{\infty}}{k T}$ equals 3.
Fig. E.13 Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \Phi_\infty}{kT}$ equals 3.5.
Fig. E.14  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \phi_{\infty}}{kT}$ equals 4.
Fig. E.15  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_e e \phi_\infty}{kT}$ equals 4.5.
Fig. E.16  Computed concentration distribution in a medium, $C(x,y,t)$, when $\frac{z_i e \phi_\infty}{kT}$ equals 5.
Appendix F

MATLAB code for use of the Finite Difference Method

F.1 Application of the Forward Difference Method to Concentration Distribution for Bulk Diffusion (Chapter V)

clear script -for3
clear T nx nt Length k h L a Re wO w Dev
format long

T=1
nx=100
nt=1465
k=T/nt
Length=6.4
h=Length/nx
L=k/(h^2)

a(1,1)=1-2*L;
a(1,2)=L;
for i=2:nx-2,
a(i,i)=1-2*L;
a(i,i+1)=L;
a(i,i-1)=L;
end
a(nx-1,nx-1)=1-2*L;
a(nx-1,nx-2)=L;

w0(nx-1,1)=0;
w=a*w0;
w(1,1)=w(1,1)+L*0.5;
w0=w;

for j=2:nt,
w=a*w0;
w(1,1)=w(1,1)+L;
w0=w;
end
for ii=1:nx-1,
    Re(ii,1)=1-erf(h*ii/2);
end
Re

for i=1:nx-1,
    Dev(i,1)=Re(i,1)-w(i,1);
end
Dev

save wfor3.dat w /ascii
save Refor3.dat Re /ascii
save Devfor3.dat Dev /ascii
F.2 Application of the Crank-Nicolson Method to Concentration Distributions for Bulk Diffusion (Chapter V)

clear script -CN3
clear T nx nt Length k h L a b c d Re w0 w Dev
format long

T=1
nx=100
nt=1465
k=T/nt
Length=6.4
h=Length/nx
L=k/(h^2)

a(1,1)=1+L;
a(1,2)=-L/2;
for i=2:nx-2,
a(i,i)=1+L;
a(i,i+1)=-L/2;
a(i,i-1)=-L/2;
end
a(nx-1,nx-1)=1+L;
a(nx-1,nx-2)=-L/2;

b(1,1)=1-L;
b(1,2)=L/2;
for i=2:nx-2,
b(i,i)=1-L;
b(i,i+1)=L/2;
b(i,i-1)=L/2;
end
b(nx-1,nx-1)=1-L;
b(nx-1,nx-2)=L/2;

c(1,1)=L/2*(0.5+1);
c(nx-1,1)=0;

d=inv(a);
w0(nx-1,1)=0;
w=d*(b*w0+c);
w0=w;
c(1,1)=L;
for j=2:nt,
w=d*(b*w0+c);

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w0=w;
end
w

for ii=1:nx-1,
    Re(ii,1)=1-erf(h*ii/2);
end
Re

for i=1:nx-1,
    Dev(i,1)=Re(i,1)-w(i,1);
end
Dev

save wCN3.dat w /ascii
save ReCN3.dat Re /ascii
save DevCN3.dat Dev /ascii
F.3 Application of the Crank-Nicolson Method to Calculation of Concentration Distributions around a Grain Boundary with an Adjacent Space Charge Potential (Chapter IV)

F.3.1 Using Hyperbolic Potential Term, Eqn. (4.6)

```
clear script -gb6002
clear Lx Lx1 Ly T nx nx1 ny nt h1 h2 k l c0 y t Bdum1 Bdum2 x A B i i j

clear al b1 c1 d1 e1 a2 b2 c2 d2 e2 AA AAT BB CC DD DD1 DD2 w0 w z0

z0=5;
Lx=6;
Lx1=1;
Ly=15;
T=1;
nx=30;
nx1=20;
ny=30;
nt=1000;
h1=Lx1/nx1
h2=(Lx-Lx1)/(nx-nx1)
k=Ly/ny
l=T/nt

for i=1:nx1+1,
    x=(i-1)*h1;
    Bdum1=-4*atanh(exp(-x)*tanh(-z0/4));
    Bdum2=4*tanh(-z0/4)/exp(x)/(1-(tanh(-z0/4))^2/exp(2*x));
    A(i)=Bdum2*exp(Bdum1);
    B(i)=exp(Bdum1);
end

for i=nx1+2:nx,
    x=Lx1+(i-nx1-1)*h2;
    Bdum1=-4*atanh(exp(-x)*tanh(-z0/4));
    Bdum2=4*tanh(-z0/4)/exp(x)/(1-(tanh(-z0/4))^2/exp(2*x));
    A(i)=Bdum2*exp(Bdum1);
    B(i)=exp(Bdum1);
end

for i=1:nx1,
    a1(i)=A(i)*1/4/h1-B(i)*1/2/(h1^2);
    b1(i)=-B(i)*1/2/(k^2);
    c1(i)=1+B(i)*1/(h1^2)+B(i)*1/(k^2);
```
\[ d1(i) = -B(i) \times \frac{1}{2(k^2)}; \]
\[ e1(i) = A(i) \times \frac{1}{4(h1-B(i)) \times \frac{1}{2(h1^2)}; \]
end

\begin{align*}
\text{i} &= \text{nx1+1;} \\
\text{a1(i)} &= \text{A(i) \times h2^2 \times \frac{1}{2}} \times \text{(h1-h2^2+h1^2*h2) - B(i) \times h2 \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)}; \\
\text{b1(i)} &= \text{-B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{c1(i)} &= \text{1-A(i) \times (h2^2-h1^2) \times \frac{1}{2}} \times \text{(h1*h2^2+h1^2*h2) - B(i) \times h1 \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)} + \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{d1(i)} &= \text{-B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{e1(i)} &= \text{-A(i) \times h1^2 \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)} - \text{B(i) \times h1 \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)}; \\
\end{align*}

for \( i = \text{nx1+2:nx}, \)
\begin{align*}
\text{a1(i)} &= \text{A(i) \times \frac{1}{4}} \times \text{h2-B(i) \times \frac{1}{2}} \times \text{(h2^2)}; \\
\text{b1(i)} &= \text{-B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{c1(i)} &= \text{1+B(i) \times \frac{1}{2}} \times \text{(h2^2)+B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{d1(i)} &= \text{-B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{e1(i)} &= \text{-A(i) \times \frac{1}{4}} \times \text{h2-B(i) \times \frac{1}{2}} \times \text{(h2^2)}; \\
\end{align*}
end

for \( i = \text{1:nx1}, \)
\begin{align*}
\text{a2(i)} &= \text{-A(i) \times \frac{1}{4}} \times \text{h1+B(i) \times \frac{1}{2}} \times \text{(h1^2)}; \\
\text{b2(i)} &= \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{c2(i)} &= \text{1-B(i) \times h1 \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{d2(i)} &= \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{e2(i)} &= \text{A(i) \times \frac{1}{4}} \times \text{h1+B(i) \times \frac{1}{2}} \times \text{(h1^2)}; \\
\end{align*}
end

\begin{align*}
\text{i} &= \text{nx1+1;} \\
\text{a2(i)} &= \text{-A(i) \times h2^2 \times \frac{1}{2}} \times \text{(h1-h2^2+h1^2*h2) + B(i) \times h2 \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)}; \\
\text{b2(i)} &= \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{c2(i)} &= \text{1+A(i) \times (h2^2-h1^2) \times \frac{1}{2}} \times \text{(h1*h2^2+h1^2*h2) - B(i) \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)} - \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{d2(i)} &= \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{e2(i)} &= \text{A(i) \times h1^2 \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)} + \text{B(i) \times h1 \times \frac{1}{2}} \times \text{(h1^2*h2+h1*h2^2)}; \\
\end{align*}

for \( i = \text{nx1+2:nx}, \)
\begin{align*}
\text{a2(i)} &= \text{-A(i) \times \frac{1}{4}} \times \text{h2+B(i) \times \frac{1}{2}} \times \text{(h2^2)}; \\
\text{b2(i)} &= \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{c2(i)} &= \text{1-B(i) \times \frac{1}{2}} \times \text{(h2^2)-B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{d2(i)} &= \text{B(i) \times \frac{1}{2}} \times \text{(k^2)}; \\
\text{e2(i)} &= \text{A(i) \times \frac{1}{4}} \times \text{h2+B(i) \times \frac{1}{2}} \times \text{(h2^2)}; \\
\end{align*}
end

\begin{align*}
\text{j} &= 1; \\
\text{for} \ i = (j-1) \times (ny-1)+1:j \times (ny-1), \\
\text{AA(i,i)} &= \text{c1(j);} \\
\text{AA(i+ny-1,i)} &= \text{a1(j+1);} \\
\text{end} \\
\text{for} \ i = (j-1) \times (ny-1)+1:j \times (ny-1)-1, \\
\text{AA(i+1,i)} &= \text{b1(j);} \\
\text{AA(i,i+1)} &= \text{d1(j);} \\
\text{end} \\
\text{j} &= 2;
for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) \),
\[
AA(i, i) = c1(j);
\]
\[
AA(i-ny+1, i) = e1(j-1) + a1(j-1);
\]
\[
AA(i+ny-l, i) = a1(j+1);
\]
end
for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) - 1 \),
\[
AA(i+1, i) = b1(j);
\]
\[
AA(i, i+1) = d1(j);
\]
end
end

for \( j = 3:nx-1 \),
for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) \),
\[
AA(i, i) = c1(j);
\]
\[
AA(i-ny+1, i) = e1(j-1);
\]
\[
AA(i+ny-l, i) = a1(j+1);
\]
end
for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) - 1 \),
\[
AA(i+1, i) = b1(j);
\]
\[
AA(i, i+1) = d1(j);
\]
end
end

\[ j = nx; \]

for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) \),
\[
AA(i, i) = c1(j);
\]
\[
AA(i-ny+1, i) = e1(j-1);
\]
\[
AA(i+ny-l, i) = a1(j+1);
\]
end
for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) - 1 \),
\[
AA(i+1, i) = b1(j);
\]
\[
AA(i, i+1) = d1(j);
\]
end

\[ \text{AAT=AA}'; \]
\[ \text{DD1=AAT*AA}; \]
\[ \text{DD2=inv(DD1)}; \]
\[ \text{clear DD1} \]
\[ \text{DD=DD2*AAT}; \]
\[ \text{clear DD2} \]
\[ \text{clear AAT} \]
\[ \text{clear AA} \]

\[ j = 1; \]

for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) \),
\[
BB(i, i) = c2(j);
\]
\[
BB(i+ny-l, i) = a2(j+1);
\]
end
for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) - 1 \),
\[
BB(i+1, i) = b2(j);
\]
\[
BB(i, i+1) = d2(j);
\]
end

\[ j = 2; \]

for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) \),
\[
BB(i, i) = c2(j);
\]
\[
BB(i-ny+1, i) = e2(j-1) + a2(j-1);
\]
\[
BB(i+ny-l, i) = a2(j+1);
\]
end
for \( i = (j-1) \cdot (ny-1) + 1 \cdot j \cdot (ny-1) - 1 \),
\[
BB(i+1, i) = b2(j);
\]
\[
BB(i, i+1) = d2(j);
\]
end
BB(i+1,i) = b2(j);
BB(i,i+1) = d2(j);
end

for j=3:nx-1,
    for i=(j-1)*(ny-1)+1:j*(ny-1),
        BB(i,i) = c2(j);
        BB(i-ny+1,i) = e2(j-1);
        BB(i+ny-1,i) = a2(j+1);
    end
    for i=(j-1)*(ny-1)+1:j*(ny-1)-1,
        BB(i+1,i) = b2(j);
        BB(i,i+1) = d2(j);
    end
end

j=nx;
for i=(j-1)*(ny-1)+1:j*(ny-1),
    BB(i,i) = c2(j)+e2(j);
    BB(i-ny+1,i) = e2(j-1);
end
for i=(j-1)*(ny-1)+1:j*(ny-1)-1,
    BB(i+1,i) = b2(j);
    BB(i,i+1) = d2(j);
end

w0(1,1) = 0;
w0(nx*(ny-1),1) = 0;

CC(nx*(ny-1),1) = 0;
for i=1:nx,
    ii=(i-1)*(ny-1)+1;
    CC(ii,1) = CC(ii,1)+0.5*b2(i)-b1(i);
end
w=DD*(BB*w0+CC);
w0=w;

for j=2:nt,
    j
clear CC
    CC(nx*(ny-1),1) = 0;
    for i=1:nx,
        ii=(i-1)*(ny-1)+1;
        CC(ii,1) = CC(ii,1)+b2(i)-b1(i);
    end
    w=DD*(BB*w0+CC);
w0=w;
end

w

save wgb6002.dat w /ascii
F.3.2 Using Exponential Potential Term, Eqn. (4.42)

clear script \text{-gb7052}
clear Lx Lx1 Ly T nx nx1 ny nt h1 h2 k1 c0 y t Bdum \times A \times B \times i \times i \times j
clear a1 b1 c1 d1 e1 a2 b2 c2 d2 e2 AA BB CC DD w0 w K

K=5
Lx=6;
Lx1=1;
Ly=15;
T=1;
nx=30;
nx1=20;
ny=30;
nt=1000;
h1=Lx1/nx1
h2=(Lx-Lx1)/(nx-nx1)
k=Ly/ny
l=T/nt

for i=1:nx1+1,
x=(i-1)*h1;
Bdum=K*exp(-x);
A(i)=-Bdum*exp(Bdum);
B(i)=exp(Bdum);
end

for i=nx1+2:nx,
x=Lx1+(i-nx1-1)*h2;
Bdum=K*exp(-x);
A(i)=-Bdum*exp(Bdum);
B(i)=exp(Bdum);
end

for i=1:nx1,
a1(i)=A(i)*1/4/h1-B(i)*1/2/(h1^2);
b1(i)=-B(i)*1/2/(k^2);
c1(i)=1+B(i)*1/(h1^2)+B(i)*1/(k^2);
d1(i)=-B(i)*1/2/(k^2);
e1(i)=-A(i)*1/4/h1-B(i)*1/2/(h1^2);
end

i=nx1+1;
a1(i)=A(i)*h2^2*1/2/(h1*h2^2+h1^2*h2)-B(i)*h2*1/(h1^2*h2+h1*h2^2);
b1(i)=-B(i)*1/2/(k^2);
c1(i)=1-A(i)*h2^2-1/2/(h1*h2^2+h1^2*h2)+B(i)*(h1+h2)*1/(h1^2*h2+h1*h2^2)+B(i)*1/(k^2);
d1(i)=-B(i)*1/2/(k^2);
e1(i)=-A(i)*h1^2*1/2/(h1^2*h2+h1*h2^2)-B(i)*h1*1/(h1^2*h2+h1*h2^2);
for i=nx1+2:nx,
a1(i)=A(i)*1/4/h2-B(i)*1/2/(h2^2);
\[ \begin{align*}
\text{bl}(i) &= -B(i) \frac{1}{2}(k^2); \\
\text{cl}(i) &= 1 + B(i) \frac{1}{2}(h^2) + B(i) \frac{1}{2}(k^2); \\
\text{dl}(i) &= -B(i) \frac{1}{2}(k^2); \\
\text{el}(i) &= -A(i) \frac{1}{4}h^2 - B(i) \frac{1}{2}(k^2); \\
\end{align*} \]

\text{end}

\text{for } i = 1: \text{nxl},
\begin{align*}
\text{a2}(i) &= -A(i) \frac{1}{4}h^2 + B(i) \frac{1}{2}(h^2) + B(i) \frac{1}{2}(k^2); \\
\text{b2}(i) &= B(i) \frac{1}{2}(k^2); \\
\text{c2}(i) &= 1 - B(i) \frac{1}{2}(h^2) - B(i) \frac{1}{2}(k^2); \\
\text{d2}(i) &= B(i) \frac{1}{2}(k^2); \\
\text{e2}(i) &= A(i) \frac{1}{4}h^2 + B(i) \frac{1}{2}(h^2); \\
\end{align*}

\text{end}

i = \text{nxl} + 1;
\begin{align*}
\text{a2}(i) &= -A(i)h^2 + B(i) \frac{1}{2}(h^2) + B(i) \frac{1}{2}(k^2); \\
\text{b2}(i) &= B(i) \frac{1}{2}(k^2); \\
\text{c2}(i) &= 1 + B(i) \frac{1}{2}(h^2) - B(i) \frac{1}{2}(k^2); \\
\text{d2}(i) &= B(i) \frac{1}{2}(k^2); \\
\text{e2}(i) &= A(i) \frac{1}{4}h^2 + B(i) \frac{1}{2}(h^2); \\
\end{align*}

\text{end}

\text{AA}(n*(ny-1), n*(ny-1)) = 0;

j = 1;
\text{for } i = (j-1)(ny-1) + i:j*(ny-1),
\begin{align*}
\text{AA}(i,i) &= \text{c1}(j); \\
\text{AA}(i+ny-1,i) &= \text{a1}(j+1); \\
\end{align*}

\text{end}

\text{for } i = (j-1)(ny-1) + i:j*(ny-1)-1,
\begin{align*}
\text{AA}(i+1,i) &= \text{bl}(j); \\
\text{AA}(i,i+1) &= \text{dl}(j); \\
\end{align*}

\text{end}

j = 2;
\text{for } i = (j-1)(ny-1) + i:j*(ny-1),
\begin{align*}
\text{AA}(i,i) &= \text{c1}(j); \\
\text{AA}(i-ny+1,i) &= \text{e1}(j-1) + \text{a1}(j-1); \\
\end{align*}

\text{end}

\text{for } i = (j-1)(ny-1) + i:j*(ny-1)-1,
\begin{align*}
\text{AA}(i+1,i) &= \text{bl}(j); \\
\text{AA}(i,i+1) &= \text{dl}(j); \\
\end{align*}

\text{end}

j = 3:nx-1;
\text{for } i = (j-1)(ny-1) + i:j*(ny-1),
\begin{align*}
\text{AA}(i,i) &= \text{c1}(j); \\
\text{AA}(i-ny+1,i) &= \text{e1}(j-1); \\
\end{align*}
\begin{verbatim}
AA(i+ny-1,i)=a1(j+1);
end
for i=(j-1)*(ny-1)+1:j*(ny-1)-1,
  AA(i+1,i)=b1(j);
  AA(i,i+1)=d1(j);
end
\end{verbatim}
BB(i,i)=c2(j)+e2(j);
BB(i-ny+1,i)=e2(j-1);
end
for i=(j-1)*(ny-1)+1:j*(ny-1)-1,
BB(i+1,i)=b2(j);
BB(i,i+1)=d2(j);
end
w0(1,1)=0;
w0(nx*(ny-1),1)=0;

CC(nx*(ny-1),1)=0;
for i=1:nx,
ii=(i-1)*(ny-1)+1;
CC(ii,1)=CC(ii,1)+0.5*b2(i)-b1(i);
end
w=DD*(BB*w0+CC);
w0=w;

for j=2:nt,
j
clear CC
CC(nx*(ny-1),1)=0;
for i=1:nx,
ii=(i-1)*(ny-1)+1;
CC(ii,1)=CC(ii,1)+b2(i)-b1(i);
end
w=DD*(BB*w0+CC);
w0=w;
end

w

save wgb7052.dat w /ascii
Appendix G

The Influence of the Value Specified for C(0,0) in FDM Solution of the Equation for Bulk Diffusion with Constant Surface Concentration, Eqn.(5.9)

The diffusion equation, Eqn. (5.2), has a problem of discrepancy in the limits of two variables, Eqn. (5.7) and Eqn. (5.8). To settle this problem, the average value of the two limits are taken as a value of C(0,0).

To check the validity of averaging the two limits, C(0,0) is chosen as 0 or 1, and the Forward-Difference method is performed for each case. Figure G.1 and Fig. G.2 show the error, e, the difference between the analytic solution and the numerical solution from the Forward-Difference method, as a function of scaled solute penetration, $x(4Dt)^{-1/2}$, for the cases where C(0,0) is 0 and 1, respectively. As may be seen, the effect is greater than might be expected. Most of the trends of Fig. 5.1 in the behavior of the error are lost and there is no suggestion that accurate results might be obtained for a certain value of $\lambda$ value. Almost every benefit of the Forward-Difference method is lost because just one out of 101 initial concentrations is wrong. This demonstrates that it is absolutely essential to carefully consider proper expressions for the boundary conditions and the initial conditions when the Finite Difference Method is applied.
Fig. G.1 A plot showing the effect of the setting one initial condition out of 101 wrong ($C(0,0)=0$ instead of 0.5) in the Forward-Difference method.
Fig. G.2 A plot showing the effect of the setting one initial condition out of 101 wrong ($C(0,0)=1$ instead of 0.5) in the Forward-Difference method.
Appendix H

Application of the Forward-Difference Method to a Bulk Diffusion Problem with Well-Defined Boundary Conditions

The analysis of a common bulk diffusion problem (having explicit analytical solution) with FDM in Chapter V led to the interesting observation that highly accurate results are obtained when $\lambda = 1/6$. To insure that this interesting result was not affected by two drawbacks of this particular problem, namely (1) the discontinuity of two limits of initial and boundary values, Eqn. (5.7) and Eqn. (5.8), and (2) the need for assumption of a finite boundary (= $6.4\sqrt{Dt}$) for which $C = 0$, even though the real boundary for this concentration should be located at infinity, the Forward-Difference method is applied once again to a situation especially designed so that the specification of boundary and initial conditions avoids these weak points and introduces no problem. The selected situation is as follows:

(i) The 1-dimensional diffusion equation,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

(H.1)

for $0 \leq x \leq 1$, $t \geq 0$
(ii) The boundary conditions

\[ C(0, t) = 0 \]  \hspace{1cm} (H.2)

and

\[ C(1, t) = 0 \]  \hspace{1cm} (H.3)

(iii) The initial condition

\[ C(x, 0) = \sin(\pi x) \]  \hspace{1cm} (H.4).

The analytical solution to this case can be obtained easily as

\[ C(x, t) = e^{-\pi^2 D t} \sin(\pi x) \]  \hspace{1cm} (H.5).

For convenience \( D \) is assumed as 1. The error between the analytic solution, Eqn. (H.5), and the value obtained from the Forward-Difference method, \( e \), is illustrated in Fig. H.1, for the case where \( t \) equals 0.5.

The behavior is similar to Fig. 5.1. In other words, as \( \lambda \) becomes smaller the error decreases but below a certain value of \( \lambda \), the error once again becomes larger. This is exactly the situation displayed in Fig. 5.1. The maximum error, \( e_{\text{max}} \), which occurred when \( x \) equals 0.5, is monitored as a function of \( \lambda \) in Fig. H.2. It also displays a perfect linear relationship as does Fig. 5.3. The linear regression result is as follows;

\[ e_{\text{max}} = -2.91911 \times 10^{-6} + 1.751369 \times 10^{-5} \lambda \]  \hspace{1cm} (H.6)

\[ R = 0.999999998 \]
The regression result verifies the perfect linear relationship between $\lambda$ and the maximum error, and also confirms that at $\lambda = 1/6$ the maximum error is zero, which means that the error equals zero for the entire range of $x$. To confirm the fact, the error is evaluated for $\lambda = 1/6$ and illustrated in Fig. H.3 along with the data presented in Fig. H.1. At this value of $\lambda$ the actual maximum error is $\sim 10^{-12}$ and the maximum relative error is $\sim 10^{-6}\%$, which verifies that the Forward-Difference method at this $\lambda$ value gives as accurate a result as the analytic solution. From this application to a well defined situation, it has been confirmed that the result of this study of Chapter V did not come from a strange coincidence but represents real characteristic of the Forward-Difference method.
Fig. H.1  The variation of error between the Forward-Difference method and an analytic solution, $e$, as a function of $x$ with various $\lambda$ values.
Fig. H.2 Result of the least square fitting between the maximum error and $\lambda$. 
Fig. H.3 A plot showing that when $\lambda$ equals $1/6$ there is no noticeable error for all $x$ range when the Forward-Difference method is applied.
Bibliography


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