FIRST PRINCIPLE CALCULATIONS OF DEFECT STRUCTURES IN ZINC OXIDE

By

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An undergraduate thesis submitted in partial fulfillment of
the requirements for the degree of

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NATIONAL INSTITUTE OF PHYSICS
University of the Philippines - Diliman

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FIRST PRINCIPLE CALCULATIONS OF DEFECT STRUCTURES IN ZINC OXIDE

Abstract

by Christian Loer T. Llemit, BS
University of the Philippines - Diliman
March 2020

: Roland V. Sarmago

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Dedication

This dissertation/thesis is dedicated to my mother and father who provided both emotional and financial support

Chapter One

INTRODUCTION

1.1 Purpose and Motivation

Describe the importance of defects in ZnO

1.2 Objectives

Study the mechanisms of different defects in ZnO

1.3 Outline

This is an example of how to cite [1]

Chapter Two

Review of Related Literature

2.1 Semiconductors

2.1.1 Properties

2.1.2 Applications of Semiconductors

2.1.3 Defects in Semiconductors

2.2 Zinc Oxide

describe ZnO in broad perspective

2.2.1 Crystal Structure

Consider different phases

2.2.2 Crystallographic Directions and Planes

2.2.3 Brillouin Zone Symmetry

2.2.4 Photoluminescence Properties

2.2.5 Defects

Chapter Three

THEORETICAL FRAMEWORK

3.1 Electronic Structure

The problem of electronic structure methods begins with the attempt to solve the general non-relativistic time-independent Schrödinger equation given as

$$\hat{\mathcal{H}}\Psi = E\Psi \tag{3.1}$$

where $\hat{\mathcal{H}}$ is the Hamiltonian operator for a system of electrons, Ψ is the electronic wavefunction and E is the energy of the system. Consider a single electron in three dimensional system, the Schrödinger equation can be expressed as

$$\hat{\mathcal{H}}\Psi_n = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi_n + V\Psi_n = \epsilon_n\Psi_n \tag{3.2}$$

where m is the mass of electron, V is the effective potential energy and ϵ_n is the energy of electron in the orbital. The term orbital denotes the solution of the Schrödinger equation for a system of only one electron. This will be useful in later sections because this will allow to distinguish between the exact quantum state of a system of N interacting electrons from the approximate quantum state of N electrons in N orbitals, where each orbital is a solution to one-electron wavefunction in (3.2). If V is zero for the case of free electrons (i.e. non-interacting), then the orbital model is exact.

Since electrons are restricted by the potential inside the atom, the simplest way of solving (3.2) is by considering an infinite potential well. The electrons are confined inside a cube of length L where the potential V inside is zero and infinite at outside must satisfy the boundary condition

$$\Psi_n(L_x, L_y, L_z) = 0 \tag{3.3}$$

where L_x, L_y, L_z can be either 0 or L. The solution will have a sine dependence

$$\Psi_n(x, y, z) = \sqrt{\left(\frac{2}{L}\right)^3} \, \sin\!\left(\frac{n_x \pi}{L} x\right) \sin\!\left(\frac{n_y \pi}{L} y\right) \sin\!\left(\frac{n_z \pi}{L} z\right) \tag{3.4}$$

where n_x, n_y, n_z are integer quantum states. Provided that $k_i = n_i \pi / L$ where $i = x, y, \text{or}\, z$; then the energy dispersion relation can be expressed as

$$\epsilon_k = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} k^2 \propto k^2 \tag{3.5}$$

Note that energy levels are discretized by the quantum states which arises from imposing the boundary conditions.

3.1.1 Electronic Band structure

Inside the crystal lattice, the periodic arrangement of atoms or ions causes the potential to be periodic which eventually gives rise to the formation of energy bands. The wavefunction Ψ will become periodic in space with a period L and must obey the Born-von Karman boundary condition

$$\Psi_k(x, y, z) = \Psi_k(x + L, y, z) \tag{3.6}$$

and similarly for the y and z coordinates. It can be shown that wavefunctions satisfying (3.2) and (3.6) are the Bloch form of a travelling plane wave

$$\Psi_k(\vec{\mathbf{r}}) = u_k(\vec{\mathbf{r}}) \exp\!\left(i \vec{\mathbf{k}} \cdot \vec{\mathbf{r}}\right) \tag{3.7}$$

where $u_k(\vec{\mathbf{r}})$ has the period of the crystal lattice with $u_k(\vec{\mathbf{r}}) = u_k(\vec{\mathbf{r}} + \vec{\mathbf{R}})$. Here $\vec{\mathbf{R}}$ is the translation vector which can be simply thought as the periodicity expressed as vector. The Bloch expression can be written as

$$\begin{aligned}\Psi_k(\vec{\mathbf{r}} + \vec{\mathbf{R}}) &= u_k(\vec{\mathbf{r}} + \vec{\mathbf{R}}) \exp\Big(i\vec{\mathbf{k}} \cdot (\vec{\mathbf{r}} + \vec{\mathbf{R}})\Big) \\ \Psi_k(\vec{\mathbf{r}} + \vec{\mathbf{R}}) &= u_k(\vec{\mathbf{r}}) \exp\Big(i\vec{\mathbf{k}} \cdot \vec{\mathbf{r}}\Big) \exp\Big(i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}\Big) \\ \Psi_k(\vec{\mathbf{r}} + \vec{\mathbf{R}}) &= \Psi_k(\vec{\mathbf{r}}) \exp\Big(i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}\Big) \qquad (3.8)\end{aligned}$$

Notice that the wavefunction differs from the plane wave of free electrons only by a periodic modulation given by the new phase factor. This means that the electrons in the crystal lattice are treated as perturbed weakly by the periodic potential of the ion cores.

3.1.1.1 Band structure of free electron

A special case of periodicity is where the potential is set to zero, which is applicable for the free electrons. The wavefunction will be a plane wave

$$\Psi_k(\vec{\mathbf{r}}) = \exp\Big(i\vec{\mathbf{k}} \cdot \vec{\mathbf{r}}\Big) \qquad (3.9)$$

that represents travelling wave with a momentum $\vec{\mathbf{p}} = \hbar\vec{\mathbf{k}}$. The energy dispersion relation is still given by (3.5) but this time the allowed energy values are distributed essentially from zero to infinity. Figure 3.1 shows the parabolic dependence of energy with the wavevector k. Since the system is periodic in real space, it must be true for the reciprocal space, in this cae by $2\pi/a$ where a is some lattice constant. Figure 3.1a shows the extended zone scheme where there are no restrictions on the values of wavevector $\vec{\mathbf{k}}$. When wavevectors are outside the first Brillouin zone (BZ), they can be translated back to the first zone by subtracting a suitable reciprocal lattice vector. In mathematical sense

$$\vec{\mathbf{k}} + \vec{\mathbf{G}} = \vec{\mathbf{k}}' \qquad (3.10)$$

where $\vec{\mathbf{k'}}$ is the unrestricted wavevector, $\vec{\mathbf{k}}$ is in the first Brillouin zone, and $\vec{\mathbf{G}}$ is the translational reciprocal lattice vector. The energy dispersion relation can always be written as

$$\begin{aligned}\epsilon(k_x, k_y, k_z) &= \frac{\hbar^2}{2m}(\vec{\mathbf{k}} + \vec{\mathbf{G}})^2 \\ &= \frac{\hbar^2}{2m}[(k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2] \end{aligned} \tag{3.11}$$

Figure 3.1b shows the reduced zone scheme where the bands are folded into the first BZ by applying (3.10). Any energy state beyond the first BZ is the same to a state inside the first BZ with a different band index n.

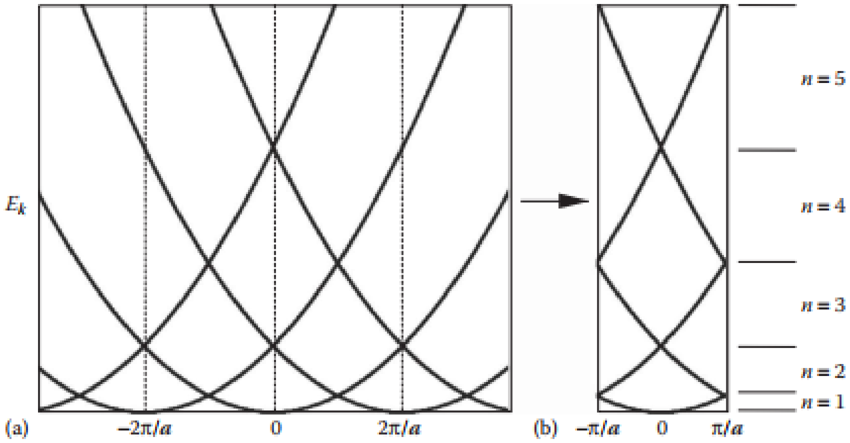

Figure 3.1 Free electron band structure

3.1.1.2 Band structure of electrons in solids

When atoms are very far from each other with no interaction, each electron occupies specific discrete orbitals such as 1s, 2p, 3d, etc. When they are bring closer enough, the outermost (valence) electrons interact with each other and will result in the energy level splitting. The innermost (core) electrons remain as they are, since they are closer to the nuclei and bounded by a deep potential well. For a solid containing a large N atoms, there will be N orbitals (i.e. N 3d-orbitals) trying to occupy the same energy level. Pauli's exclusion principle will prevent this from happening, hence what happens is there will be splitting of the energy level and eventually forms a band. Figure 3.2 summarizes the evolution of energy levels as the atoms are brought together.

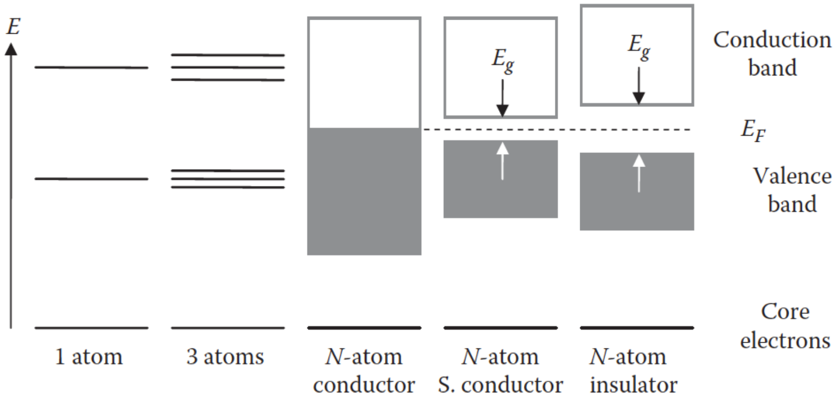

Figure 3.2 Formation of bands and band gaps when isolated atoms are bring closer together

Another interesting property of band structure is the formation of energy band gaps. This happens when the valence electrons interact with the periodic potential of the nuclei. Assuming a weak periodic potential, most of the band structure will not changed very much, except possibly at the Brillouin zone boundaries with a wavevector of $\vec{\mathbf{k}} = n\pi/a$. The orbitals with the wavevector at zone boundaries, chosen to be at high symmetry points, follows the Bragg diffraction condition and thus are diffracted. The valence electrons are scattered (or reflected) at the zone boundary in which the wavefunction are made up of equal plane waves travelling from the left and from the right. The wavefunction becomes a standing wave that resembles more of those bound states. Hence, there will be a forbidden region where travelling waves are not allowed. If sufficient energy is provided to the electron, they can overcome the binding potential.

insert the symmetry points in IBZ.

3.1.2 Density of States

explains fermi dirac distribution

3.1.3 Projected Density of States

3.2 Many-body Quantum Mechanics

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3.2.1 Time Independent Schrödinger Equation

3.2.2 Simplifying Assumptions

3.2.3 Use of Atomic Units

3.2.4 Hamiltonian Operator

3.2.5 Indistinguishability of electrons

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3.3.3 Hartree-Fock Method

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3.4.3 Kohn Sham (KS) Formalism

3.4.3.1 KS Equation

3.4.3.2 Energy Terms

3.4.4 Self Consistent Field Calculation

3.5 Exchange-correlation Functional

Chapter Four

DFT Calculation of Solids

4.1 Basis Sets

4.1.1 Plane Wave

4.1.2 Gaussian Orbital

4.1.3 Slater type orbitals

4.2 Pseudopotential Approach

This is sample text

4.2.1 Freezing the core electrons

4.2.2 Pseudizing the valence electrons

4.2.3 Common Pseudopotentials

4.2.3.1 Norm-Conserving PP

4.2.3.2 Ultrasoft PP

4.2.3.3 Projector Augmented Wave

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4.3.2.3 Irreducible Brillouin Zone

4.3.3 k-point sampling

4.3.3.1 Monkhorst-Pack method

4.3.3.2 Gamma Point Sampling

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4.4 Bloch Representations

4.4.1 Electrons in solid

4.4.2 Bloch Theorem in periodic systems

4.4.3 Fourier Expansion of Bloch representations

4.4.3.1 Fourier Expansions

4.4.3.2 Fast Fourier Transformation (FFT)

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4.6.1 Band Structure of free electrons

4.6.2 Band Structure of electrons in solids

4.6.3 Electronic Density of States

4.7 Practical Aspects

Chapter Five

Software Implementation

5.1 QUANTUM ESPRESSO

5.1.1 MKL Libraries

5.1.2 PWSCF routines

cbands, cegterg, cdiaghg

5.2 Intel Compilers

5.3 Executables

5.4 Computational Details

5.4.1 Convergence Testing

5.4.2 Hubbard correction parameters

5.4.3 Supercell creation

5.4.4 Slab Model

5.4.5 Structural relaxation

5.4.6 scf calculation

5.4.7 bandstructure calculation

5.4.8 dos calculation

DOST COARE

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2. Wetterstrand, K. A. *DNA Sequencing Costs: Data from the NHGRI Genome Sequencing Program (GSP)* www.genome.gov/sequencingcosts.

APPENDIX

Appendix A

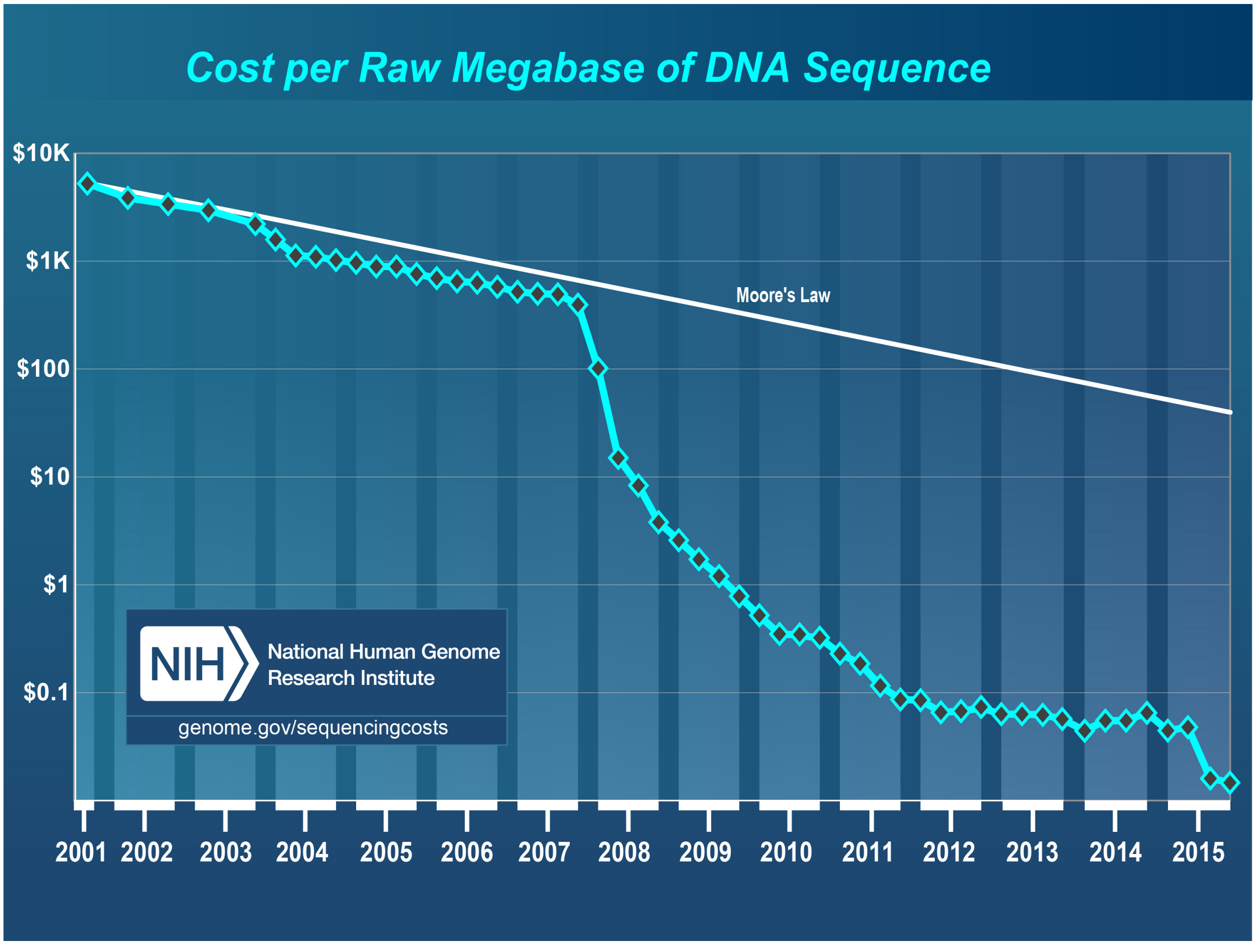

Figure A.1 Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

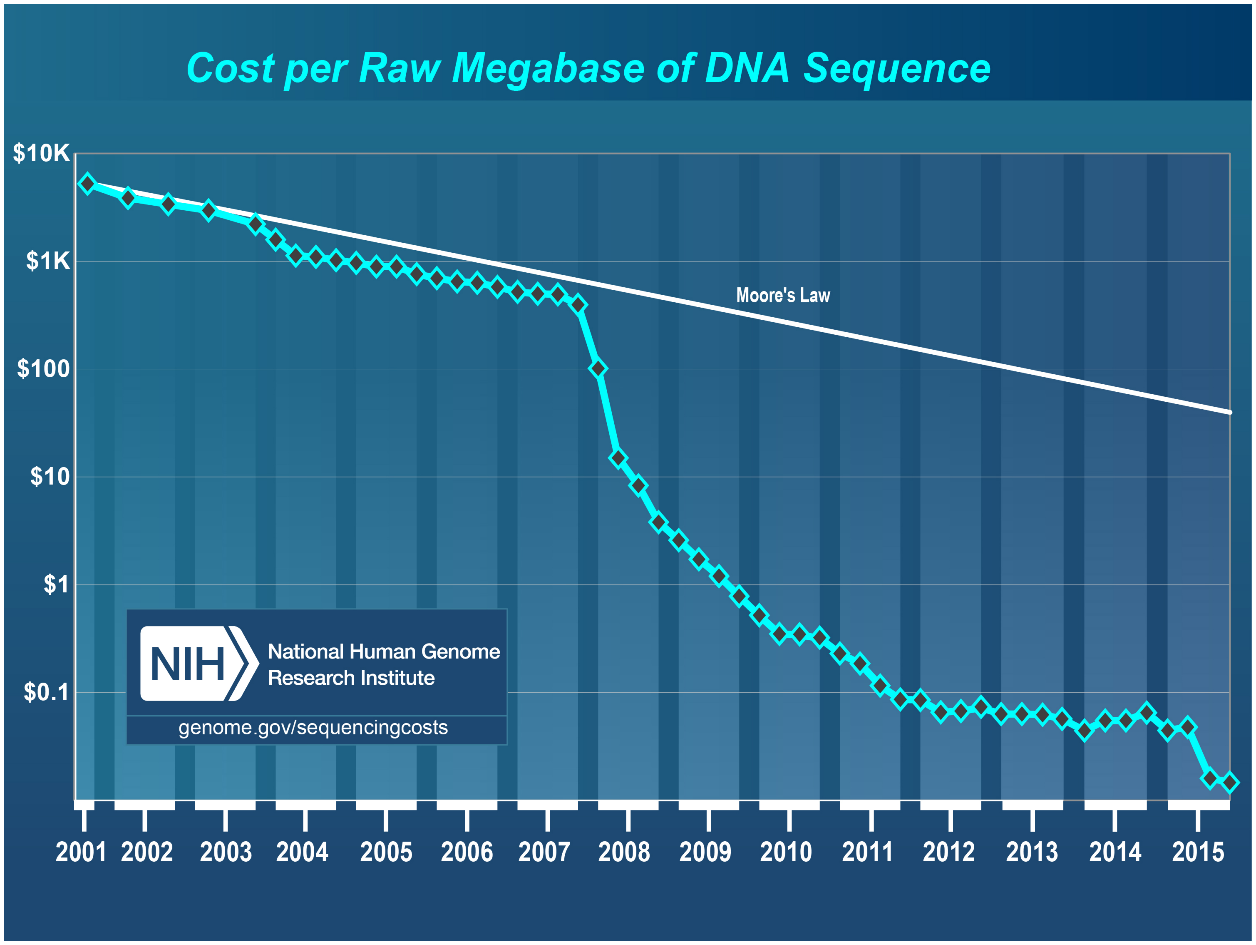

Figure A.2 Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

Appendix B

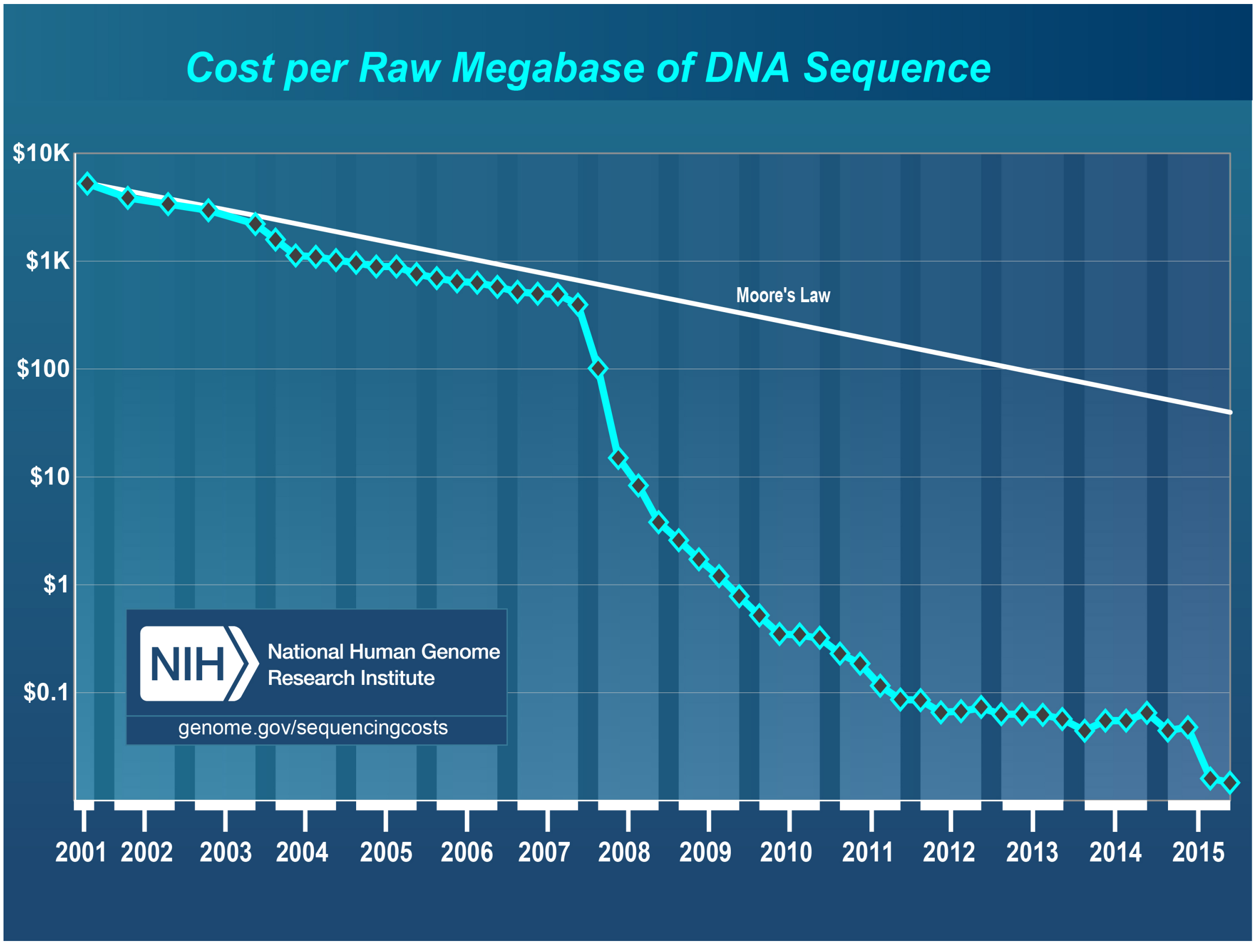

Figure B.1 Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

Appendix C

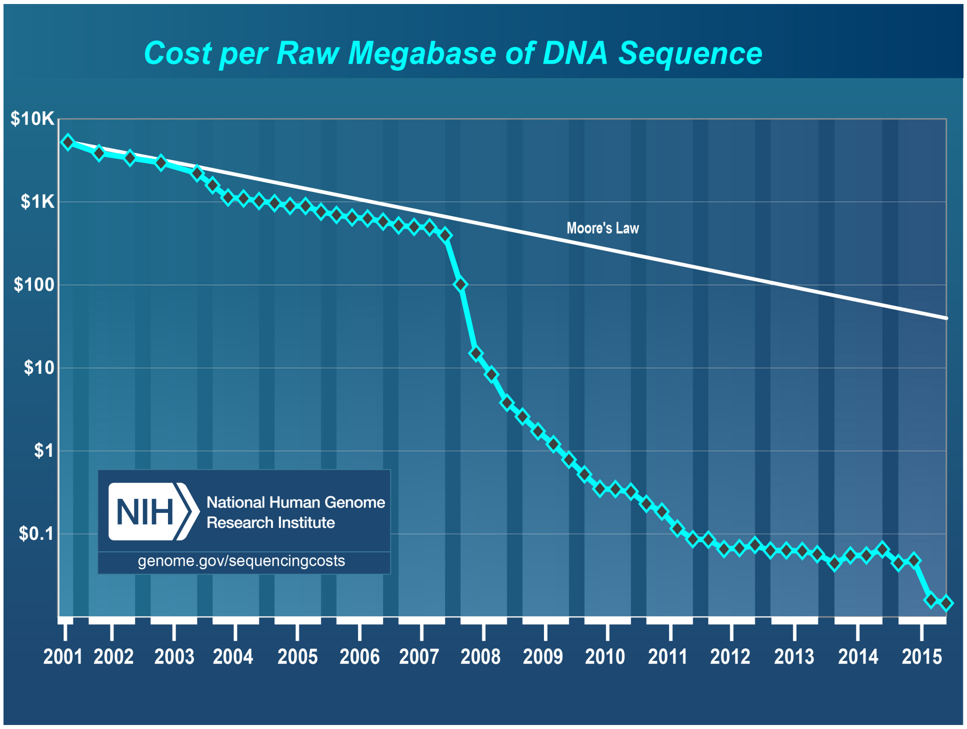

Figure C.1 Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

Appendix D

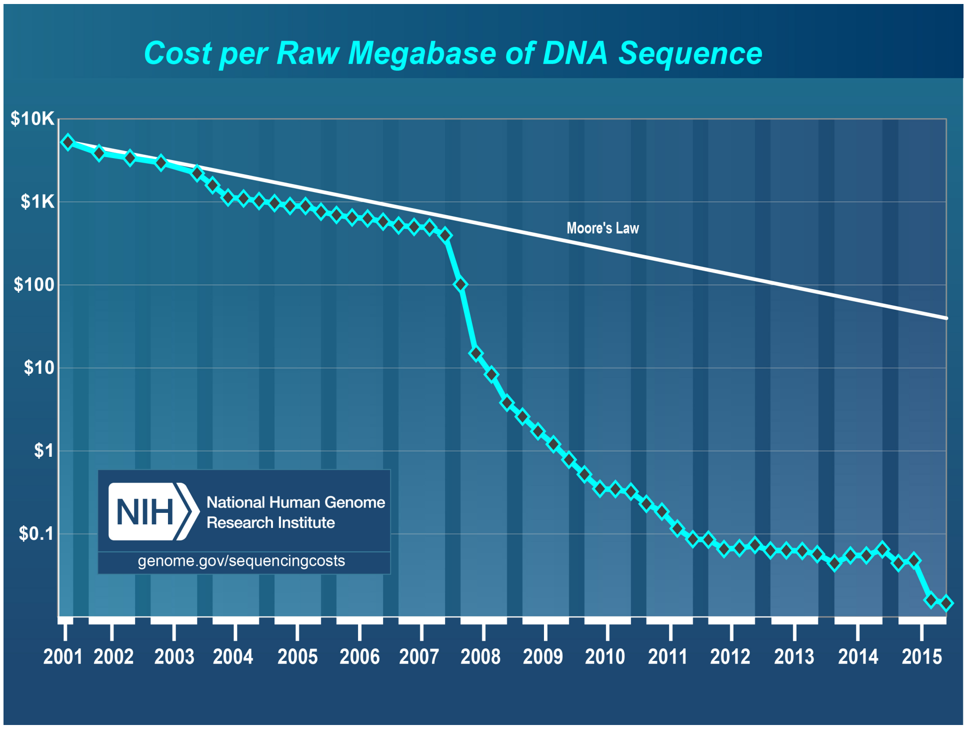

Figure D.1 Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

Appendix E

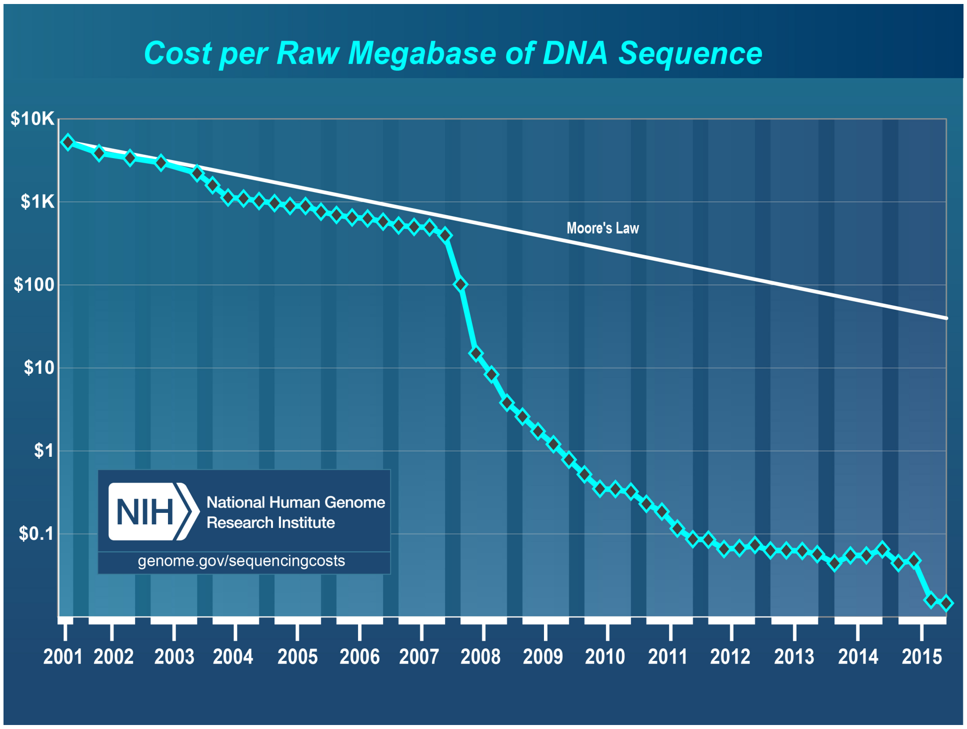

Figure E.1 Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]