Chapter 1 Introduction

1.1 General Introduction

"There's plenty of room at the bottom" is the title of a classic talk given on December 29, 1959, in which the great physicist Richard Feynman introduced a new field of physics to the annual meeting of the American Physical Society at the California Institute of Technology. Over 40 years ago, Feynman imagined a new physical world of ultra-small volumes and highlighted some difficulties that researchers might encounter when visiting it. His talk provided a vision for engineers and scientists to establish a new field, which—with subsequent developments in novel equipment and manufacturing skills—is know known as "nanotechnology."

In recent years nanotechnology has become one of the most important and exciting forefront field in physics, chemistry, engineering and biology which the characteristic dimensions are below ca. 1000 nm. It shows great promise for providing us in the near future with many breakthroughs that will change the direction of technological advances in a wide range of applications. This kind of work is often called nanotechnology. Sub-micron lithography is clearly very profitable—ask anyone who uses a computer—but it is equally clear that conventional lithographic techniques will not let us prepare semiconductor devices in which individual dopant atoms are located at specific lattice sites. Although computer hardware capability has exhibited steady exponential growth for the last 50 years—and there is a fairly widespread belief that these trends are likely to continue for at least several more years—conventional lithographic techniques are beginning to reach their limits.

As semiconductor devices become scaled down to ever-smaller sizes within the nano-regime, a variety of technological and economic problems arise, the rules of classical physics give way to quantum mechanics, and the term “molecular-scale” becomes more accurate than “nanoscale.” At this point, the scaling of sizes that has successfully reduced device features from the microscale to the nanoscale reaches its limits, and, therefore, alternative manufacturing methods, materials, device structures, and architectures are required.

1.2 Zero-Dimensional Nanostructure

Zero-dimensional nanostructure, called nanodot, or nanoparticle, a wide range of materials—including a variety of organic and biological compounds, inorganic oxides, metals, and semiconductors— has attracted growing interest due to their realization in functional structures and in the field of nano-devices such as optoelectronics, information storage, and sensing [1-5]. Because nanodots have 10^6 atoms or less, their properties differ from those of the same atoms bonded together to form bulk materials. Nanodots are generally considered to be a number of atoms or molecules bonded together with a radius of < 100nm. They can build by assembling individual atoms or subdividing bulk materials. What makes nanodots very interesting and endows them with their unique properties is that their size is smaller than critical length that characterizes many physical phenomena. Generally, physical properties of materials can be characterized by some critical length, a thermal diffusion length, or scattering length, for example. The electrical conductivity of a metal is strongly determined by distance that electrons travel between collisions with the vibrating atoms or impurities of the solid. This distance is called the mean free path or the scattering length. If the sizes of nanodots are less than this characteristic length, it is possible that new physics or chemistry may occur.

1.3 Top-Down Nanotechnology

Pushed by the ever-growing needs of information technology for smaller and smaller logic and memory devices on one hand and scientific curiosity about behavior of matter on small length scales on the other, nanoscience has developed into one of the most active fields of research worldwide. A very attractive feature of these activities is the strong tendency towards interdisciplinary cooperation. This becomes immediately apparent in the context of the development and testing of various approaches to preparing nanostructures, often referred to as the development of nanolithographies.

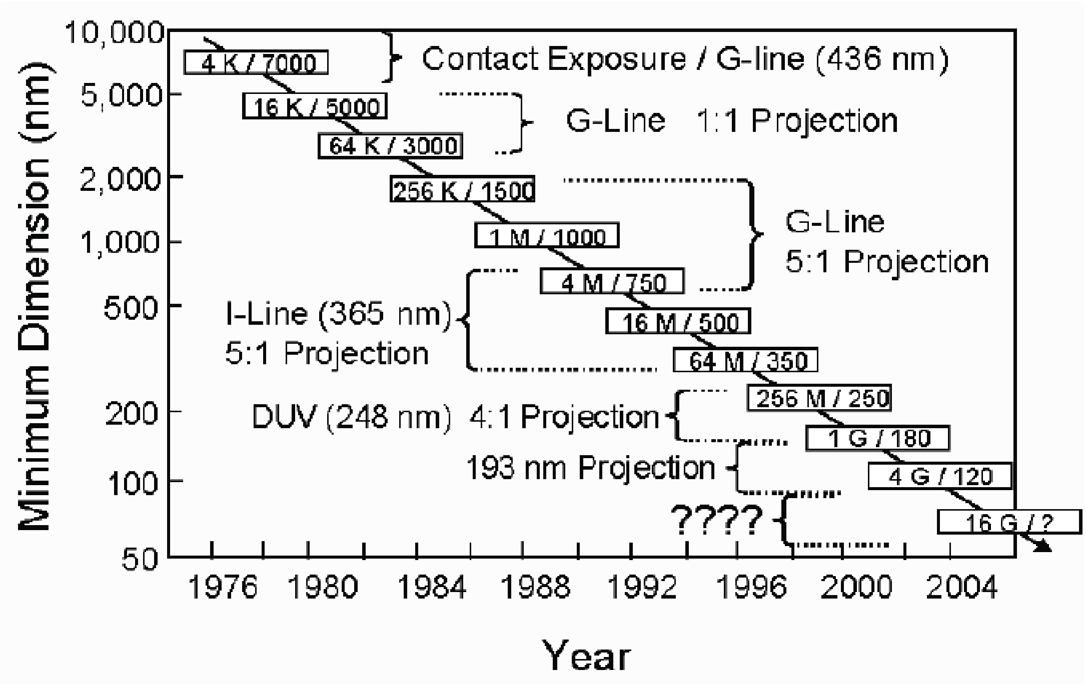

Figure 1.1 The semiconductor industry roadmap of memory technologies and the associated lithographic technologies used to manufacture each generation of devices. Each box displays each device generation’s memory size and critical feature size (nm).

The lithography technology used to define each generation of circuit pattern has an enormous influence on the industrial manufacturing process. Figure 1.1 displays the semiconductor industry roadmap of memory technologies and their associated lithographic technologies [6]. In the early days, the wavelength of the light source used was that of the G-line (436 nm), who's critical size was ca. 750 nm. Subsequently, the I-line (365 nm) was used. Currently, 193- and 157-nm radiation is the main source of exposure light. Table 1.1 lists the semiconductor industry roadmap of the key node indicators in the years 1999–2005 and three-year predictions for subsequent years through 2014 [7].

The fabrication of high-performance integrated circuits requires increasingly shorter wavelengths of the radiation source to manufacture devices of decreasing critical sizes. Optical lithography technologies face a bottleneck for the formation of etched patterns over the next 10–15 years because the critical size of the patterns depends on the wavelength of the exposing radiation source [8]. When the wavelength of the radiation source reaches its physical limit, it will become difficult and expensive to prepare pattern having, for example, 5–20-nm line widths. Despite the invention of some impressive techniques that increase process resolution—such as the use of phase shift masks (PSM)[9-10] and liquid immersion lithography (LIL)[11]—the limits of these methods to support process fabrication have been predicted to be ca. 65–90 nm. Therefore, emergency lithography technologies—including electron beam direct writing (EBDW) [12-13], extreme ultraviolet (EUV) lithography [14], electron beam projection lithography (EPL) [15] and ion beam projection lithography (IPL) [16]—have all been introduced for the fabrication of electronic devices. These approaches are all potential "next-generation lithography" (NGL) technologies, but currently they remain expensive and difficult to operate and implement.

Nanoimprinting (Figure 1.2) is an emerging lithographic technology that has promise for the high-throughput patterning of nanostructures. Based on the mechanical embossing principle, the nanoimprinting technique can achieve pattern resolutions beyond the limitations set by light diffraction or e-beam scattering in other conventional techniques. The nanoimprinting lithography (NIL) technique [17-18] involves two main steps. The first requires electron beam direct writing on an e-beam resist, followed by the deposition of metal and reactive ion etching, to define a pattern on a mold. Secondly, the mold is imprinted upon the substrate, which has a coated resist, and then metal deposition and RIE etching allows the preparation of 2D or 3D nanostructures.

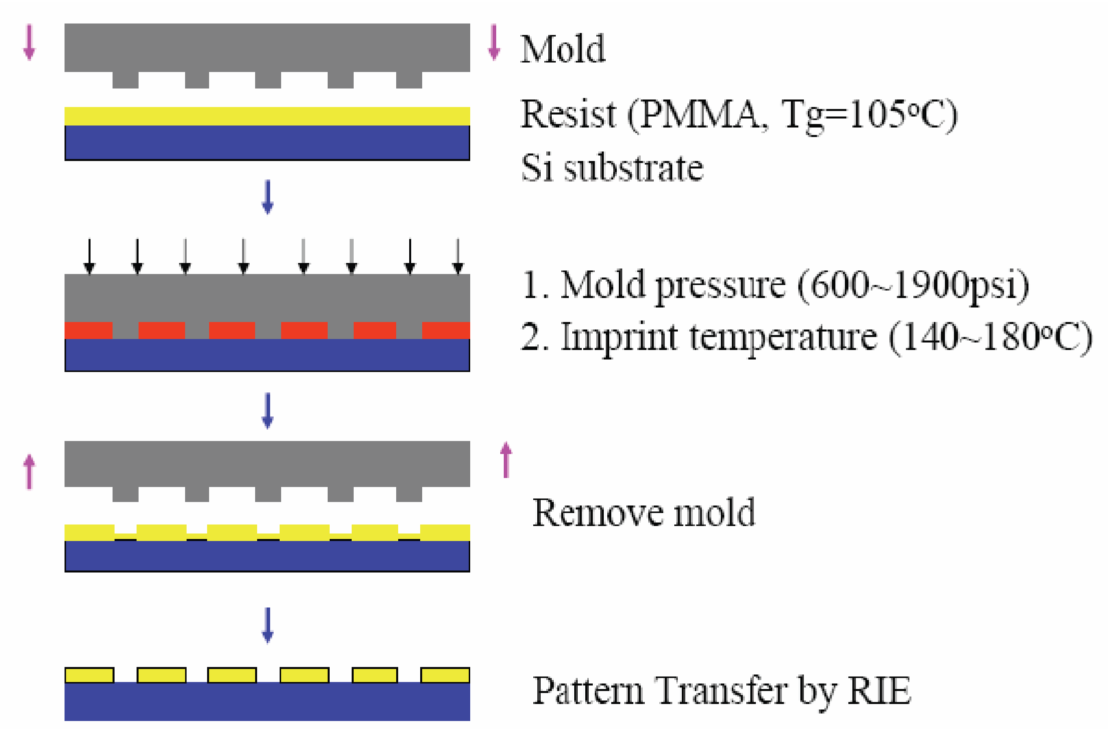

Figure 1.2 The nanoimprinting process [18]

The lithographic methods described above all have resolutions of 100 nm or better, but each of these methods has its limitations: diffraction effects during optical lithography, proximity effects during EBDW and EPL, difficulties in mask fabrication for X-ray and EUV lithographies, difficulties in aligning and preparing vertical structures during soft lithography and NIL, and stochastic space charge during ion projection lithography.

1.4 Bottom-Up Nanotechnology

Figure 1.3 displays the two general methods available for producing nanosized materials. The first (the top-down approach) starts with a bulk material and then break it into smaller pieces using mechanical, chemical, or other forms of energy. The opposite, bottom-up approach is to synthesize the material from atomic or molecular species through chemical reactions that allow the precursor particles to grow in size. Both approaches can be performed in the gas or liquid phases, supercritical fluids, the solid state, or under vacuum.

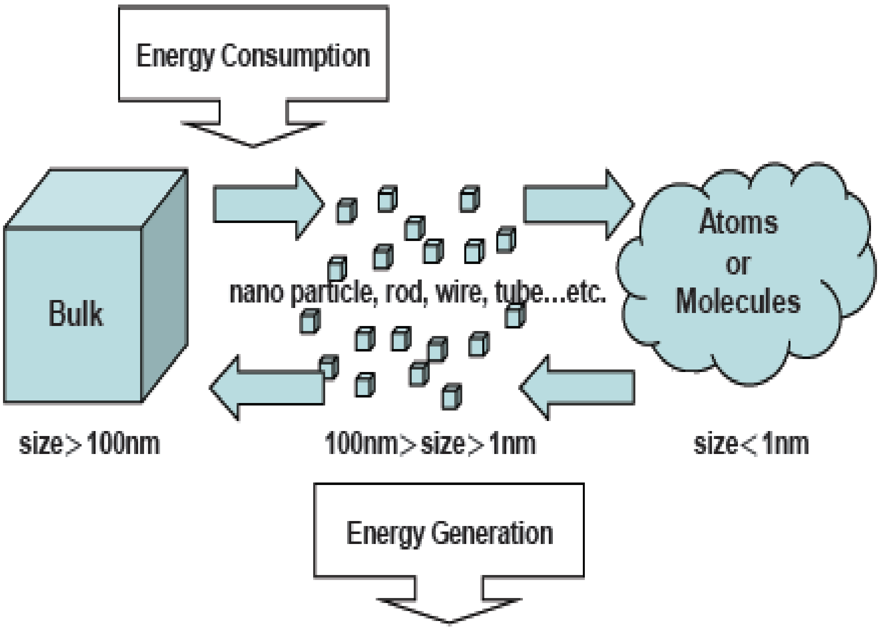

Figure 1.3 Two basic approaches toward the fabrication of nanomaterials: top-down (from left to right) and bottom-up (from right to left).

Section 1.4 introduces some of the fabrication methods that may be used to shrink the sizes of physical scale. A completely different approach, often referred to as bottom-up, relies on the self-organization of larger molecules used as building blocks for the resulting nanostructures. The term “bottom-up” means that the nano-components (particles, nanotubes, and nanowires) are synthesized from single molecules, whereas the top-down process fabricates these nano-components from bulk materials. Methods to produce nanoparticles from atoms are chemical processes based on transformations in solution e.g. sol-gel processing, chemical vapour deposition (CVD), plasma or flame spraying synthesis, laser pyrolysis, atomic or molecular condensation. These chemical processes rely on the availability of appropriate “metal-organic” molecules as precursors. Sol-gel processing differs from other chemical processes due to its relatively low processing temperature. This makes the sol-gel process cost-effective and versatile. In spraying processes the flow of reactants (gas, liquid in form of aerosols or mixtures of both) is introduced to high-energy flame produced for example by plasma spraying equipment or carbon dioxide laser. The reactants decompose and particles are formed in a flame by homogeneous nucleation and growth. Rapidly cooling results in formation of nanoscale particles.

Two general ways are available to control the formation and growth of the nanoparticles. One is called arrested precipitation, and this technique depends either on exhaustion of one of the reactants or on the introduction of the chemical that would block the reaction. Another method relies on a physical restriction of the volume available for the growth of the individual nanoparticles by using templates.

The sol gel technique is a long-established industrial process for the generation of colloidal nanoparticles from liquid phase, which has been further developed in last years for the production of advanced nanomaterials and coatings. Sol-gel-processes are well adapted for oxide nanoparticles and composites nanopowders synthesis. The main advantages of sol-gel techniques for the preparation of materials are low temperature of processing, versatility, and flexible rheology allowing easy shaping and embedding.

Aerosol-based processes are a common method for the industrial production of nanoparticles. Aerosols can be defined as solid or liquid particles in a gas phase, where the particles can range from molecules up to 100 μm in size. Aerosols were used in industrial manufacturing long before the basic science and engineering of the aerosols were understood. Traditionally, spraying is used either to dry wet materials or to deposit coatings. Spraying of the precursor chemicals onto a heated surface or into the hot atmosphere results in precursor pyrolysis and formation of the particles.

The theory of condensation for the production of metal nanopowders is well known. This method is used mainly for metal containing nanoparticles. A bulk material is heated in vacuum to produce a stream of vaporised and atomised matter, which is directed to a chamber containing either inert or reactive gas atmosphere. Rapid cooling of the metal atoms due to their collision with the gas molecules results in the condensation and formation of nanoparticles. These particles are liquid since they are still too hot to be solid. The liquid particles collide and coalesce in a controlled environment so that the particles grow to specification, remaining spherical and with smooth surfaces. At this point the nanoparticles are very reactive, so they are coated with a material that prevents further interaction with other particles or with other materials. If a reactive gas like oxygen is used then metal oxide nanoparticles are produced.

Nanoparticles of a wide range of materials - including a variety of organic and biological compounds, but also inorganic oxides, metals, and semiconductors - can be processed using chemical self-assembly techniques. These techniques exploit selective attachment of molecules to specific surfaces, biomolecular recognition and self-ordering principles as well as well-developed chemistry for attaching molecules onto clusters and substrates and other techniques like reverse micelle, sonochemical, and photochemical synthesis to realise 1-D, 2-D and 3-D self-assembled nanostructures. The molecular building blocks act as parts of a jigsaw puzzle that join together in a perfect order without an obvious driving force present.

Long-term and visionary nanotechnological conceptions, however, go far beyond these first approaches. This applies in particular to the development of biomimetic materials with the ability of self-organisation, self-healing and self-replication by means of molecular nanotechnology. One objective here is the combination of synthetic and biological materials, architectures and systems, respectively, the imitation of biological processes for technological applications. This field of nanobiotechnology is at present still in the state of basic research, but is regarded as one of the most promising research fields for the future.

1.5 Motivation

Many metal oxide nanodot arrays which have wide band gap such as TiO_2, In_2O_3, ZnO and SnO_2 etc. have attracted because of functional structures and in the field of nano-devices such as optoelectronics, information storage, and sensing. The top-down technologies can provide for a great deal, rapid and low-priced process to fabricate nanodot arrays. In this report, we propose a novel strategy for fabricating the metal oxide nanodot arrays with anodic alumina film to serve as the template. Anodizing reaction proceeds in the sequence of growth of porous anodic alumina when the aluminum layer is consumed up to the underlying metal, growth of metal oxide under the bottoms of the alumina pores occurred. Using this approach, we can achieve highly ordered arrays of metal oxide nanodots with a narrow size distribution and the controllable size.