

## Introduction

In Greek, the word “nano” means “small” or “dwarf.” In the scientific literature, nano is a prefix that refers to “one-billionth,” that is  $10^{-9}$  of the scale it modifies. One nanometer (nm) is very small, approximately 1/100,000 to 1/50,000 of a single strand of human hair, or about one-half to one-third of the width of DNA, or as wide as a few atoms. Nanotechnology is concerned with this size range, starting from 1 up to 100 nm. Its definition comes from the National Nanotechnology Initiative (NNI; see <http://www.nano.gov>) as (a) creation and use of structures, devices and systems that have novel properties and functions; (b) ability to pattern and build structures and systems starting at molecular range up to one-hundred nanometer level; and (c) ability to control processes at nanometer range for advanced material processing and manufacturing [167, 168]. Building structures and processes in this nano-realm requires a better understanding of new physics, chemistry and engineering, which maybe significantly different than the established approaches used for macro-systems. Only after that, extensive applications of *micro/nanomachining* or *nanomanufacturing* would be realized.

Recent advances in the science and engineering have significantly impacted the art of building small things, which in turn has led to many innovations. The very same advances have also helped shrink the size of electronic chips, while allowing them to process a larger amount of data much faster. The famous Moore’s law dictates that the speed of processors doubles every eighteen months, which corresponds to a 1,000 fold increase in the number of transistors crammed in the same area every fifteen years. In 1975, the number of devices integrated on a chip with the area of one quarter of square inch was about 3,000. This number steadily climbed up to one million in 1990 and to more than one billion in 2006 (see Intel website <http://www.intel.com/technology/mooreslaw/> for the most recent numbers).

The Moore law has proven to be valid for the last four decades; yet with decreasing feature size its predictive ability is being challenged [138]. The corollary of Moore’s law (a.k.a. Rock’s law) is about the cost of manufacturing of these devices, which states that the investment into the infrastructure

of fabrication facilities would increase two-fold in every three years. The cost of new facilities and procedures are likely to be prohibitive as we approach nanoscale feature sizes. And, the challenge will always be there to push the limit of building small to the edge, which currently borders about 65 nm for silicon technologies [162], targeted down to 45 nm soon (Intel 2007). The challenges of new science, new technology, and new manufacturing paradigms at the nanoscale are clear cut, which necessitate further experimental and theoretical studies.

The realm of nanotechnology is in the so-called mesoscale regime, a regime that lies between the classical domains of engineering where bulk properties and continuum formulations hold, and the molecular regime where quantum mechanics dominate. Only during the last decade or so, physics, chemistry and biology and their interactions have started to be unraveled within this nanoworld. Still, the underlying concepts and the required thermophysical properties are not readily available for successful implementation of nanomanufacturing ideas.

As with any other manufacturing process, the success of nanomanufacturing does not only depend on understanding the relevant science, but also the extent of its art, or the successful implementation of engineering principles to make each and every process reliable with precision and repeatability. This requirement goes hand in hand with the development of predictive capabilities to simulate the processes of nanomanufacturing before actually building the systems. These computational models are also crucial to bringing more science to the art of nanotechnology, which is growing in leaps and bounds. Among all, the material processing and material removal requires a better understanding of the energy transfer mechanism by electrons and laser/light beams, and how the energy is dispersed at the nanometer scale to generate small patterns in a predictable way.

The concept and promise of nanotechnology are covered in several scientific books and monographs, starting from Eric Drexler's *Engines of Creation* [49]. Since then, many other studies have been devoted to nanosciences and nanotechnology, including those recent more technical titles by Kohler and Fritzsche [102], Chen [30], Mansoori [123], Bhushan [18], Roduner [169], Dupas et al. [50], Zhang [222], as well as the easy-to-read accounts for non-scientists by Ratner and Ratner [163] and Booker and Boysen [23]. A recent review of the National Nanotechnology Initiative [206] is also quite useful as it outlines how the NNI has shaped the research and development efforts so far and what the expectations are in future efforts.

In this monograph, we mainly focus on conceptual tools to describe thermal transport inside a gold workpiece due to an impinging electron beam. Two other texts, by Chen [30] and Zhang [222] provide extensive coverage of transport phenomena as related to nanoscale devices and processes. Our objective here is more specific. We will outline the underlying physics, governing equations and the numerical models that can be used for understanding and simulations of "top-down" nanomanufacturing processes. The primary

emphasis here will be on energetic electrons (emitted from nanoscaled tips) and micro/nanomachining based on electron-matter interactions, although many of the principles discussed can readily be used for laser-based machining applications as well. As mentioned before, we focus only on the particle theories and leave the discussion of wave approaches to other references. The detailed experimental validations of these concepts are also left to other accounts.

## 1.1 Motivation for Building Small

There is a consensus among many researchers working in the nanoworld that the potential and challenges of nanotechnology were first heralded by Richard Feynman in his famous 1959 talk titled “There is plenty of room at the bottom” [54]. He wonderfully articulated the concept of building small and inscribing on a piece of dust all the words ever written within all the books published at that time. Feynman’s insight is considered to have given birth to what we now call nanotechnology. Yet, it is well-known that the concepts of atoms and electrons have been discussed by mankind since ancient Greeks, when Lucretius, Democritus, and Epicurus played with the idea and its potential implications back in the first century BC on the shores of Aegean Sea. Nevertheless, the atomic world was simply “imagined” until the beginning of the nineteenth century, when the scientific theories were firmly established by Dalton, Lavoisier, Gay-Lussac, among others. And only in the beginning of the twentieth century were electrons actually “seen” with the help of experiments conducted by Thompson. This was a major breakthrough, as it led to the development of electron microscopy and impacted the atomic scale visualization. That very same discovery was the starting point of Feynman’s articulations, as he suggested the use of electrons as tools and probes. Another major discovery was made in 1982 with the development of the scanning tunneling microscopy (STM) by Binnig and Rohrer [20,21]. The underlying principle of STM is the quantum mechanical phenomena of tunneling which enables the visualization of subatomic domains in conducting surfaces. After that, the path to innovation was firmly paved, and the introduction of NNI in 2000 simply helped to put the further development on solid ground.

Nanomanufacturing is one of the main thrust areas of nanotechnology, as recently stated by the National Research Council on their review of the NNI [206]. In general, nanomanufacturing can be viewed either as a top-down or bottom-up process. In the former, one can manipulate the matter using an external source to create patterns as small as a few nanometers wide. In the latter, the intrinsic and natural properties of molecules themselves can be used to guide them to form new structures with novel properties for different applications. Self assembly is a paradigm of bottom-up processes, and the engine of nanobiotechnology [132], which is another thrust area of NNI. Nanobiotechnology encompasses the building blocks of living organisms

and fundamental of materials and materials processing, and is likely to have major impact on every aspects of our lives [132, 206].

With the advances in metrology and instrumentation, nanomanufacturing and nanomachining are likely to be important engines of the nanotechnology revolution. A recent search in Web-of-Knowledge in March 2008 revealed significant surge of interest in “nanopatterning,” “nanomachining,” and “nanomanufacturing.” A keyword search for “nanomachining” returned 130 papers, whereas 1,140 publications were found for “nanopatterning.” Most of these papers have only been published during the last few years. The earliest accounts, however, trace back to 1988 [147] and 1993 [114]. Still, these numbers of citations are very small compared to more than 1900 hits obtained for “nano-lithography” as a topic keyword and more than 22,500 publications for “self-assembly.”

## 1.2 Nanopatterning Approaches

Nanometer-wide structures can be patterned using external energy sources, including laser- or ion beams, X- or gamma-rays, or electrons. Our focus in this monograph is on electron-based machining. With the recent developments and understanding of field-emission of electrons from short tips and carbon nanotubes (CNTs), there is a great potential for new micro/nanomachining procedures. Given this, we explore the thermal transfer phenomena that take place on a workpiece which is subject to incoming high-energy electron beams. Many of the theories discussed in this monograph may also be applicable to laser-beam based processing. Particularly, with the development of extreme ultraviolet lasers and further understanding of near-field radiative transfer, sub-100 nm applications will be more feasible in the near future.

Material processing with high-power and ultra-fast lasers has been explored extensively over the years for numerous industrial applications. Mega-watt lasers, with pulse durations less than 50 fs ( $10^{-15}$  s) are routinely used to produce desired structures or patterns on material surfaces, including micrometer size structures [15, 85, 111, 154, 185, 204]. Resolutions of these structures depend greatly on the incident spatial distribution of the beam. However, a laser can only be focused close to its wavelength due to the diffraction limit. This results in the limiting of the smallest resolution of the material processed by using traditional lasers with wavelengths in the visible spectrum to no less than a few hundred nanometers, or, about one-fourth to one-fifth of the laser wavelength. Therefore, it is not possible to create nanometer-scale indentations using a conventional laser machining approach based on far-field optical arrangements. However, extreme ultraviolet lasers have wavelengths in the order of 100 nm; consequently they can be used to form nanoscale structures. These processes can be analyzed with the solution of the full Maxwell equations to account for the near-field effects. In addition, recent research suggests that near-field effects can be considered using long-wavelength lasers

down to nanoscale regime (see for as example [35,65,80,203]). Yet, it is still not possible to achieve molecular level precision with light-based methodologies. Even though X- or gamma-rays may be used for molecular level machining purposes, the cost required for such applications is still prohibitive.

An alternative approach for micro/nanomachining is realized by using energized electrons bombarding the target solid and creating localized structural changes. Since electrons have wavelengths much smaller than that of electromagnetic energy involved in laser-beam processes, the diffraction effect does not play any role until a size much less than a nanometer is reached. Focusing the electron beam down to a few nanometers can be achieved by using electromagnetic lenses [51], although this is still one of the main challenges of the technology. Electron-based machining concept is likely to play more important role in the future, although most of the research has focused on electron-beam lithography (EBL) during the last three decades [125,144,187].

Nanomanufacturing is likely to continue receiving significant attention within the industry and research institutions due to the ever-growing interest in development and engineering of structures at nanometer-scale [158]. Several patterning techniques have been considered over the years for nanometer scale applications, including scanning probe approaches as summarized by Sotomayor Torres [194] and Garcia et al. [61], and listed by Bhushan [18] and Dupas et al. [50]. Among all, atomic force microscopy techniques are becoming quite attractive [70,79,213,215]. More specific examples of AFM based nanoscale patterning modalities include the dip-pen lithography of Mirkin group [64,155,172], and recent surface-wave directed self assembly approach of our group [70,71]. The extension of these approaches are collectively called scanning probe lithographies [213], which can be extended to applications for nanoscale metrology [158]. These concepts have been discussed extensively in the literature and outlined in review monographs cited above.

As we stated above, in this monograph we are limiting ourselves to mostly electron-based micro/nanomachining of metallic (gold) workpiece, although the same set of fundamental equations can be adapted for application to other materials with relative ease. Below, we provide a more detailed discussion of electron-beam processing concept.

### 1.3 Electron-Beam Processing

Electron-beam processing uses electron emission from an electron gun. During this process, a large amount of energized electrons is projected onto a solid workpiece to achieve the desirable machining process. The key requirement is the use of electrons with large kinetic energies, to allow them to penetrate through the lattice of the solid and to transfer their energy via inelastic collisions. If enough energy is deposited to a small volume, then nanoscale machining or material removal (via melting, sublimation, or ablation) can be

achieved depending on the workpiece material. The typical energies of the electrons in an electron-beam process are in the order of tens of kilo-electronvolts (keV). EBL is based on this very same concept and is relatively well established. Yet the cost associated with its infrastructure is well above \$1M, making it an exclusive approach afforded by only a few industries [18].

The electron-beam processing, as the name implies, changes the structure and the properties of a workpiece. The physics of the interaction between the impinging energetic electrons and the solid materials is very complex. As the electrons propagate inside the workpiece, they undergo a series of elastic or inelastic scatterings. Elastic scattering refers to the redirection of the propagating electron, while inelastic scattering involves both the redirection and energy attenuation of the electrons. Electrons transfer their energy to the target material by means of inelastic scatterings. Inelastic scattering in this scenario can be classified as an event where an incident electron causes the ionization of the atom by removing an inner-shell electron from its orbit producing a characteristic X-ray or an ejected Auger electron. In addition, inelastic scattering also includes the case where an electron collapses with a valence electron to produce a secondary electron [93].

Due to their small sizes, the accelerated electrons can easily penetrate the solid material through the lattices. Such penetration depends heavily upon the initial energies of electrons and their corresponding scattering patterns. Use of a highly energized electron beam assures large penetration depth for the propagating electrons, which can transfer their energies deep in the workpiece rather than just on the target surface.

There are a number of desirable features of the electron-beam processing for application to micro/nanomachining, including: (a) the possibility of finely focused electron beams, (b) the feasibility of generating high-power-density electron beams, (c) the ability to deflect electron beams rapidly and with high accuracy, and (d) the possibility of varying electron energy with acceleration voltage, hence controlling the electron penetration range. The disadvantages include (a) the necessity for high vacuum to achieve field emission (except for non-vacuum welding and electron reactive processing), (b) the generation of harmful X-rays, and (c) the difficulty in processing electrical insulators. With the recent advances in procedures to grow CNTs and manufacturing of sharp metallic tips, field-emitted electrons are more likely to be used in future micro/nanomachining applications.

Two practical application areas of electron-beam processing need further discussion. The first one is thermal processing, which includes machining, welding, annealing, and heat treatment. The second application is reactive processing, such as electron-beam processing, polymerization and depolymerization [189, 190]. The machining process is directly related to thermal processing, which is the focus of this monograph. In the following Chapters we will discuss thermal transport phenomena due to nano-tip-based machining and patterning approaches. First, we will summarize the work related to micro/nanomachining with electrons. EBL and the other nanopatterning

approaches, on the other hand, are beyond the scope of this treatise. Interested readers can refer to many recent articles and texts on the subject, including those by Marrian and Tennant [125], Stomeo et al. [187], Gates [63], Mahalik [118], Mailly [119], Garcia et al. [61], Ocola and Stein [144], Yang et al. [218], Hiemenz [73], and Woodson and Liu [213].

## 1.4 Micro/Nanomachining with Electrons

The concept of micro/nanomachining with electrons requires a clear understanding of electron and solid matter interactions, which have been investigated theoretically and experimentally by different researchers over the years. Some of these historically important theoretical works include those by Whiddington [205], Archard [7], Kanaya and Okayama [96], and Joy [93]. Almost a century ago, Whiddington [205] related the electron penetration range  $R_p$  (m) with the electron acceleration voltage  $V$  (Volt) and the mass density of the metal  $\rho$  ( $\text{kg m}^{-3}$ ), given by the following relation:

$$R_p = \frac{a V^2}{\rho}, \quad (1.1)$$

where  $a = 2.2 \times 10^{-11} \text{ kg V}^{-2} \text{ m}^{-2}$ . This is the approximate depth that the penetrating electrons can reach after they are incident on a target surface. This implies that most of the energies of the propagating electrons would be absorbed in this range, but not on the surface of the workpiece. As a result, the heating of the surface of the target cannot be achieved via direct electron bombardments, but requires heat to be conducted up from the lower layers of the solid material.

Machining of a workpiece is possible only if spatially-resolved phase change within the material can be achieved using an external energy source. Electron-beam melting has been used for practical applications for some time; however, only recently the science behind nanoscale melting is explored more thoroughly. Sánchez and Mengüç [174, 176] have discussed molecular dynamics (MD) simulations for this purpose and summarized most of the relevant work. (Chap. 9 of this monograph is devoted to the further discussion of MD approaches.)

Due to the complicated interactions between propagating electrons and the solid material, devising a physically realistic theoretical analysis of electron-beam machining is quite challenging. Electron propagation can be modeled with the electron-beam transport equation, which is usually solved using statistical approaches, such as Monte Carlo (MC) method, where a large number of electrons inside a solid material are simulated based on probability distribution functions. The desired solution is then generated according to the scorings of these electrons.

Taniguchi et al. [189] and Joy [93] argued that even with a finely focused electron beam, material processing at a very small area is difficult to achieve.



MC simulations carried out by Shimizu et al. [181] and Joy [93] suggest that the multiple scattering nature of the electron inside the solid material may cause extensive spread of electrons. However, simulations based on smaller emitters and the use of threshold heating of the workpiece show that the resolution of machining processing at nanoscale level is indeed possible [198].

The numerical approaches presented in the later chapters do not assume any probe type, but rather only the specifications of the electron beam used in the micro/nanomachining process, such as the initial beam energy, spatial beam spread, and the beam power, are important. Hence, any source of electrons that meets the required beam specifications can serve as a micro/nanomachining tool in this application.

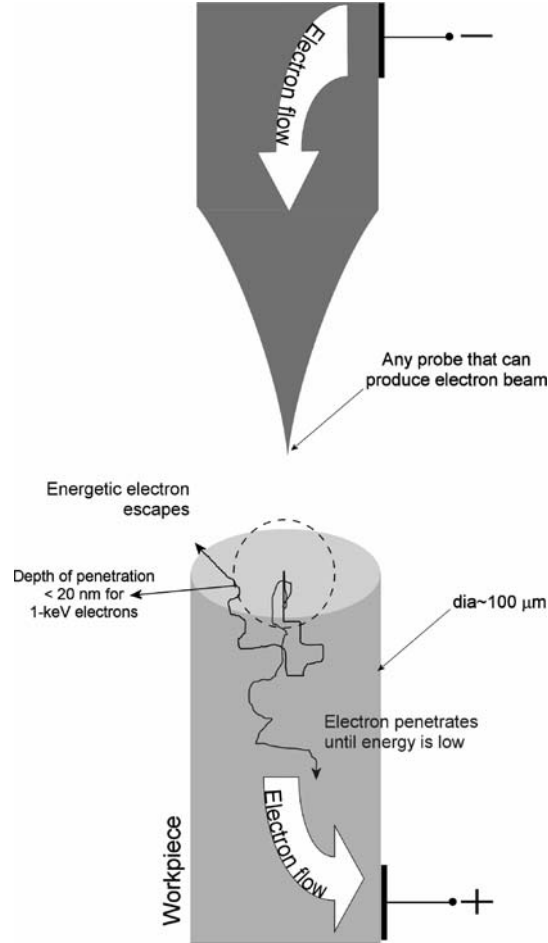
The concept of machining considered in this monograph is depicted in Fig. 1.1. As discussed above, to effectively remove atoms from the workpiece, a large amount of energy transfer from the probe via electron bombardments may be required. Depending on the probe, this may not be easy to achieve. One way to overcome this setback is to preheat the workpiece to a higher temperature through bulk heating or by the use of a laser beam. This auxiliary heating further increases the temperature of a specified location to nearly the melting point of the workpiece, where the electron bombardments occur, resulting in minimum energy required from the probe to process the material. If any field-emitted electron source is used, the electron-beam processing should be done under vacuum conditions; then the bulk heating can only be achieved by radiative or conductive transfer, but not by convective transfer.

A potential candidate for such a micro/nanomachining probe would be a CNT attached to a sharp tungsten needle (see Fig. 1.2). CNT is only one of the recently discovered carbon based nanoscale structures [82,83]. Carbon is a unique element, and takes different textures and morphologies depending on how it forms. Diamond is carbon, so are spherical fullerenes [106], spheroidal hyperfullerenes [40], cylindrical nanotubes [82], conical nanocarbon [29,179] and toroidal nanorings [126,178]. Discovered in 1991 by Sumio Iijima, CNTs proved to be very promising for a number of applications, including field emission displays [203] and for nanolithography [191]. Its field emission properties make it a very good candidate for micro/nanomachining [75,99]. The details of the production and properties of CNTs are well-documented in the literature (see, e.g., [18]); therefore there is no need to give a complete accounting about them.

Although experiments regarding the emission property of the CNTs have been performed over the years, the full range of applicability of the CNTs as machining tools remains untested. Above all, the relationships between the maximum current extracted, the maximum voltage applied, the tube diameter, and the magnification of the emitting area on the detector screen need to be addressed. Knowledge of these relationships will be required when choosing the appropriate CNTs, later discussed in this work.

The new developments in the field of CNT growth allow very intricate CNT arrays, which can be used for sequential micro/nanomachining applications.

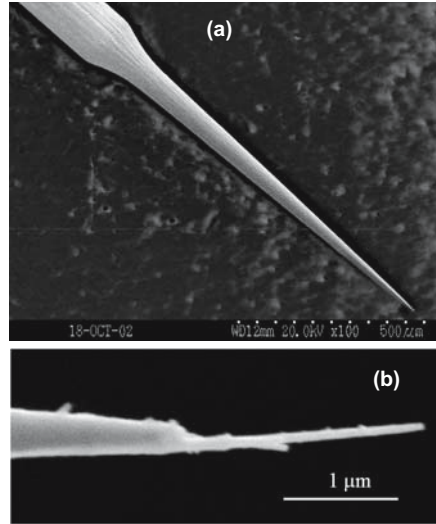




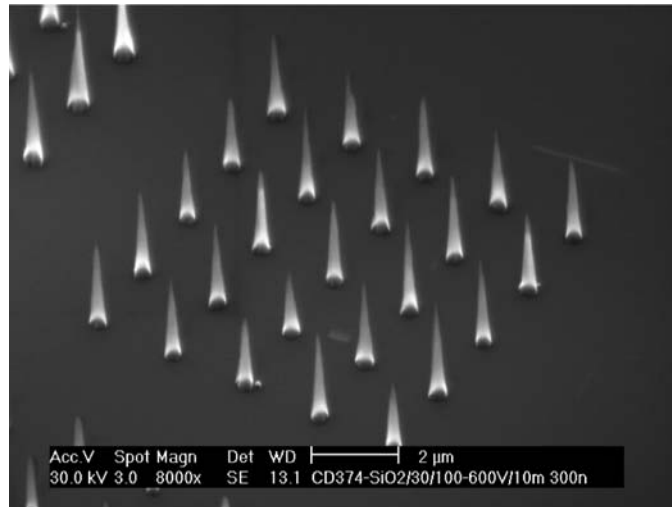
**Fig. 1.1.** A schematic of the machining process using an electron source. The figure is not drawn to the scale. The workpiece is considered to be infinite in extent compared to the electron beam. Although a voltage is applied in the figure, this is not a must for facilitating the machining process; any electron beam that can be directed towards the workpiece from an electron source is applicable here

Figure 1.3 depicts one such array [13]. Additional studies on CNT geometries will allow the development of new tools. They are discussed extensively by the Jin group [13, 14, 32–34].

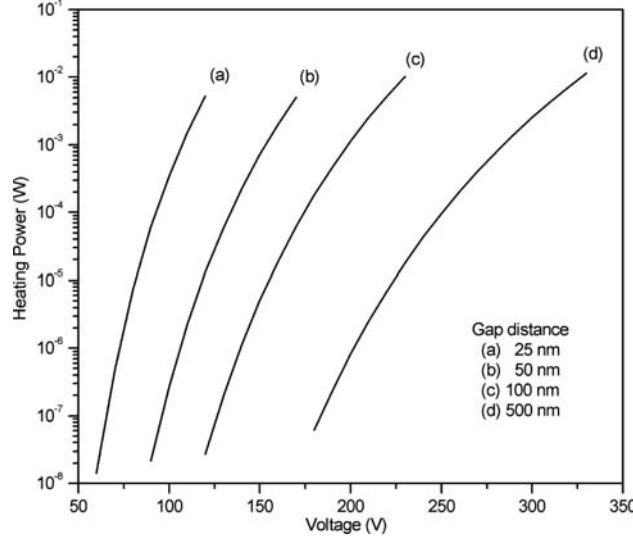
To explore the possibility of micro/nanomachining with field-emitted electrons, Sánchez et al. [177] and Sánchez and Mengüç [175] presented extensive numerical simulations. It is demonstrated that the energy available for micro/nanomachining with electrons is a function of the geometry of the CNT, i.e., its radius, length, wall thickness and the shape (open or closed), and also



**Fig. 1.2.** Structure of probe tips and mounted CNTs for demonstrating the feasibility of nano-scale probes. (a) Tungsten probe fabricated using electro-chemical etching, and (b) Enlarged view of the mounted CNT on the probe [74]



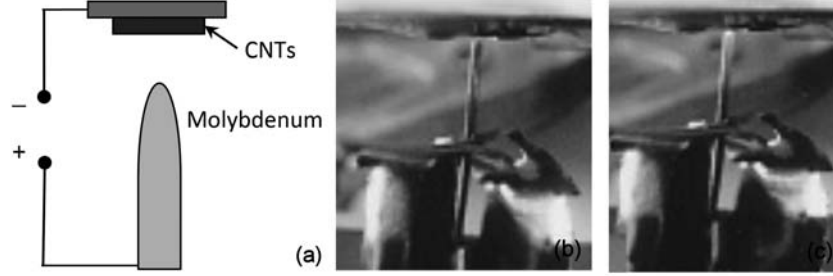
**Fig. 1.3.** An aligned and patterned periodic CNT array is shown. The array is created by *e*-beam patterning of Ni or Fe catalyst layer into islands (e.g., 50–200 nm diameters) followed by plasma CVD growth using hydrocarbon gas [13]



**Fig. 1.4.** Heating power available to the electrons emitted from a CNT with  $4\mu\text{m}$  in length,  $50\text{ nm}$  in radius,  $10\text{ nm}$  of wall thickness and a closed hemispherical tip. The heating power is calculated as a function of the gap distance (Data adapted from Sánchez et al. [177])

depends on the gap distance between the tip of the CNT and the workpiece. In Fig. 1.4 we show the effect of the gap distance on the heating power available to the emitted electrons from a CNT defined as the emission current times the applied voltage. These results indicate that as the gap distance decreases, a smaller voltage is required to achieve a given heating power. This is because of the enhancement of the field strength on the tip of the CNT as a function of the gap distance which enters in the calculation of the emission current. The available power can be further enhanced by using multiple CNTs and by focusing electrons on the workpiece. At a gap distance of  $25\text{ nm}$ , it is ideally possible to obtain power in the fraction of a milli-watt if  $100\text{ V}$  is applied, as shown in Fig. 1.4. With the use of multiple CNTs, it is indeed possible to heat a metallic workpiece to its melting temperature. Figure 1.5 depicts the experimental setup demonstrated by Jin group (Zhu et al. [223]) where they used CNTs to heat a molybdenum bar (about  $0.5\text{ mm}$  in diameter). The schematic on Fig. 1.5(a) is provided to explain the experimental pictures shown on Fig. 1.5(b) and (c). The red glowing molybdenum is at about  $1,500\text{--}2,000\text{ K}$ , as its temperature increases with the duration of the experiment.

All said, machining with electrons is likely to be one of the promising applications of nanoscale engineering, and is worth further exploration and experimental validation. Our numerical approaches presented in this monograph deal with electron-beam propagation and thermal conduction induced by an electron beam. These approaches are applicable when temperature distribution of the workpiece is desired. In addition, the type of electron



**Fig. 1.5.** (a) A schematic of the experimental setup by Jin group (Zhu et al. [223]); (b) (c) The actual experiment picture at two different times showing the red-glow of molybdenum bar heated by the field emitting CNTs

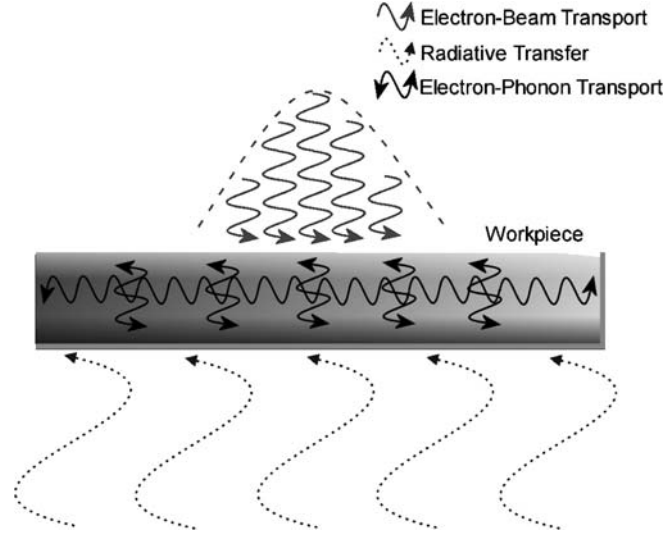
source, whether it is from an electron gun or electron field emission, does not alter the numerical approaches given in this context.

## 1.5 Outline of the Monograph

The goal in this monograph is to discuss theoretical and numerical modeling strategies mainly used for electron-beam induced thermal conduction, and hence for simulation of top-down micro- and nanomachining processes. The heat transfer mechanisms involved in these problems are electron-beam transport based on impinging electrons, coupled electron-phonon transport inside the target workpiece, and radiative energy transport when the process is assisted with a laser beam (see Fig.1.6). The predictive models for these phenomena are necessary and essential for understanding and implementation of future applications.

Starting in Chap. 2 we introduce readers to the governing equations of thermal transport for micro/nanomachining. All these derivations originate from the Boltzmann transport equation (BTE), yet based on different assumptions and simplifications. Figures 2.1 and 2.2 outline all the related transport models and their role in micro/nanomachining applications. Modeling of the BTEs for realistic physical conditions is not always straightforward. Among all solution strategies, only MC models can easily be adapted to most practical situations. For this reason, in this monograph we primarily consider the MC methods as the preferred solution techniques.

Chapter 3 is devoted to discussion of solution strategies of BTEs using MC methods, including the EBTE, the electron transport equation (ETE), and the phonon radiative transport equation (PRTE). In Chap. 4, the EBTE is further analyzed after giving the theoretical background required for its application to electron-beam based machining. In Chaps.5 and 6, we introduce additional numerical models, where MC methods for electrons are coupled



**Fig. 1.6.** Interactions of electron-beam transport, radiative transfer and electron-phonon transport shown schematically for electron-beam based micro/nanomachining, aided by auxiliary radiative heating

with two different formulations of thermal conduction problem. The Fourier law is employed in Chap. 5 to predict the temperature profile inside the workpiece. The MC method used for this purpose is called the continuous slow-down approach (CSDA), as discussed in Chap. 3. Later, in Chap. 6, the two-temperature model (TTM) is used to study the electron-phonon transport induced by an electron beam. In this case another electron-beam MC method, called the discrete inelastic scattering (DIS) method, is used.

The TTM discussed in Chap. 6 can be replaced with the electron-phonon hydrodynamic equations (EPHDEs) to account for the electrical flow and charge accumulation inside a target workpiece. This procedure is outlined in Chap. 7. In addition, a simulation procedure to predict the electronic thermal conduction using a MC method is presented, which accounts for ballistic behavior of electrons. In Chap. 8, we summarize a parallel computation procedure to allow simulation of machining based on the TTM. Different hardware architectures and their relative performances are outlined. In Chap. 9, we present the fundamentals of molecular dynamics (MD) simulations, which is important when working on isolated nano-scale and/or molecular-level patterning processes. Finally, in Chap. 10 we provide an overview of the monograph.



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